

# Statistical Transport Theory of Reacting Two-Component Fluid: Light Scattering from an $A \rightleftharpoons B$ Liquid

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A theory of light scattering from a simple  $A \rightleftharpoons B$  reacting fluid in which molecular anisotropy has been neglected is presented. The theory is a molecular-statistical one based on Mori's linear response formalism. The time-dependent correlation functions are associated with transport coefficients and the zero time correlation functions are associated with thermodynamic derivatives. The effects of the reaction are observed from both density and concentration fluctuations as well as from cross correlations between density and concentration fluctuations.

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**KEY WORDS:** Light scattering; reacting solutions; transport theory.

## 1. INTRODUCTION

The three-line Rayleigh-Brillouin spectrum of light scattered off fluids was first analyzed by Landau and Placzek<sup>(1)</sup> and more recently by Mountain<sup>(2)</sup>;

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the spectrum arises from scattering off density fluctuations whose behavior can be described in terms of thermodynamic fluctuations governed by hydrodynamic equations of motion. Among their other successes, these theories account for the Brillouin lines, spectral lines which are symmetrically displaced from the laser frequency by the sound frequency, whose linewidths vary as  $k^2$ , where  $k = (4\pi/\lambda) \sin(\theta/2)$ ,  $\lambda$  is the incident wavelength, and  $\theta$  is the scattering angle. On a molecular level these theories correspond to the coupled time evolution of density, momentum density, and energy density fluctuations<sup>(3,4)</sup>; these treatments are valid for atomic liquids provided observations are restricted to relatively small deviations from the laser frequency or, alternatively, to times which are very long compared to the times characteristic of individual molecular motions. In multicomponent liquids and in liquids composed of molecules a three-variable hydrodynamic theory is not adequate, even at long times, because of the dependence of density fluctuations upon fluctuations in concentration, internal excitations, molecular rotations, and chemical reactions. The observed spectrum is thus more complex than would be predicted from Landau and Placzek's basic theory.

The three hydrodynamic variables are conserved quantities and so exhibit very slow local fluctuations in volume elements with dimensions comparable to  $\lambda$  for visible light. In a two-component system, in the absence of chemical reactions, the concentration is also a conserved quantity, and it also exhibits slow local fluctuations. Hydrodynamic equations for two-component systems have been developed<sup>(5-10)</sup> and the spectra of such systems have been described in terms of two Brillouin (Raman) lines and two superimposed Rayleigh lines with widths which vary as  $k^2$ .<sup>(5)</sup> The concentration fluctuations are determined by the rate of interdiffusion of the species, and the theory relates these fluctuations to the diffusion constant.

For molecular liquids the choice of additional variables to describe rotations, vibrations, and reactions is less obvious because these effects cannot be described by additional slowly varying conserved quantities. Nevertheless, these modes often relax on hydrodynamic, or nearly hydrodynamic, time scales, which means that additional slowly varying, but nonconserved, quantities must be included in the theory. Appropriate variables can be introduced to describe these additional modes. Wigner rotation matrices can be used to describe rotations<sup>(11,12)</sup>; the vibrations can be described by means of the internal energy<sup>(13-15)</sup> or by a progress variable<sup>(16)</sup>; and chemical reactions have also been discussed in terms of progress variables.<sup>(17-19)</sup> Alternatively, one can describe the effects of these "internal modes" characteristic of molecular fluids in terms of hydrodynamic variables alone provided frequency-dependent transport coefficients are introduced<sup>(20)</sup>; the vibrational effects have been treated in this way by Mountain.<sup>(21)</sup> Here we shall, however, make use of the formalism in which each additional mode is associated with

an appropriate dynamical variable. Each additional mode, characterized by a single relaxation time, introduces an additional Rayleigh line into the spectrum provided that the mode is coupled to the density fluctuations. Thus if vibrations all relax with a single time, a vibrational Rayleigh line with  $k$ -independent width is observed<sup>(22)</sup>; similar results are observed for rotations.<sup>(23)</sup> For a single first-order reaction in a two-component system, the reaction is not a new mode in addition to the diffusion discussed above, but provides an alternate dissipative route for concentration fluctuations; whereas the diffusive contributions are hydrodynamic and  $k$  dependent, the reaction contribution to the Rayleigh line associated with concentration fluctuations is  $k$  independent. Both diffusion<sup>(24)</sup> and reaction<sup>(25,26)</sup> effects in the Rayleigh spectrum have been reported. One should, of course, note that the individual Rayleigh lines can be associated with specific relaxations only in certain limiting cases.

We consider a model of a fluid which consists of various "species"; these species might be distinguished by differences in polarizability, chemical structure, optical activity,<sup>(27)</sup> molecular orientation, or vibrational energy. Light is scattered off polarizability fluctuations in the fluid, or equivalently, fluctuations in the local dielectric tensor; these fluctuations could depend upon the fluctuations in the concentrations of the various "species." This dependence could arise *either because the molecular polarizability is different for the different species or because the decay of the density fluctuations depends indirectly upon the local concentrations of the various "species"*; we shall call these primary and secondary effects, respectively.<sup>(28)</sup> For the sake of simplicity we shall restrict our considerations to systems composed of two "species" only. These two species might be two chemical species, or they might be the ground and an excited vibrational state. In the following sections we develop, by means of the Mori theory,<sup>(29)</sup> hydrodynamic equations for the three conserved quantities and the concentration variable, and we express the various transport coefficients in terms of molecular quantities. We seek solutions to these equations for the light scattering spectrum and we discuss various features of the spectrum.

Before proceeding we wish to comment on the relation between our calculations and similar ones performed by others. In many ways ours are most similar in method to those of Trimble and Deutch,<sup>(9)</sup> who considered the problem of two nonreacting species. Our calculations are also similar to those of Weinberg and Oppenheim,<sup>(13)</sup> who considered internal relaxation; they did not have to take account of the possibility that the molecule in the ground and excited internal states could have different polarizabilities; in considering chemical reactions this difference in polarizabilities is important and we have included this effect. Whereas Weinberg and Oppenheim introduce the internal energy as the fourth quantity to be added to the basic set of

three conserved variables, we have introduced a concentration variable; this latter variable is a more natural choice, as we shall see, for discussing chemical reactions. Finally, because of our different way of handling expansions, we obtain rather different results for the limiting case of rapid chemical reactions or vibrational relaxation, i.e., for relaxation frequencies comparable to those of sound waves. Mountain<sup>(21)</sup> has considered the same problem as Weinberg and Oppenheim from a hydrodynamic viewpoint in which the vibrational relaxation is introduced by means of a frequency-dependent coefficient of viscosity; our results agree with those of Mountain,<sup>4</sup> even in the rapid relaxation limit, but our approach is molecular, we have introduced the vibrational or chemical relaxation in a different manner, and we have considered species with different polarizabilities. Sutherland and Deutch<sup>(10)</sup> have considered two relaxing species with different polarizabilities by a hydrodynamic technique similar to that of Mountain. Many aspects of the problem we have considered have also been treated by means of hydrodynamic approaches by Salzberg *et al.*, but we have studied a simple reaction in rather more detail. The Mori approach in terms of a concentration variable has already been applied<sup>(30,31)</sup> to reacting species but a full treatment in terms of all conserved variables has not been presented.

In an appendix we develop a technique of Mori's to relate microscopic parameters of the theory to thermodynamic quantities.

## 2. DYNAMICAL VARIABLES

Light scattering spectra probe fluctuations in the local dielectric tensor of a fluid. The dominant features of the spectrum are contained in a small frequency range  $\Delta\omega$  about the incident laser frequency, i.e.,  $(\Delta\omega)^2\tau_{\text{mol}}^2 \ll 1$ , where  $\tau_{\text{mol}}$  is a characteristic molecular time which is perhaps of the order of  $10^{-13}$  sec. The wavelength of the light used guarantees that the wave number  $k$  defined in the last section conforms to the condition  $k^2a_{\text{mol}}^2 \ll 1$ , where  $a_{\text{mol}}$  is a characteristic molecular distance which is perhaps of the order of a few angstroms; of course, for neutron diffraction this condition would not be valid and the theory developed below would not be applicable. Here we shall be interested in a scattering theory for which  $k$  and  $\omega$  are very small and times are long, i.e., we shall be interested in hydrodynamic (and not molecular) distances, frequencies, and times.

<sup>4</sup> Mountain has shown that slight differences occur in the light scattering formulas obtained by incorporating the effects of an internal degree of freedom by means of a fourth variable or mode and by means of a frequency-dependent viscosity; these differences arise because of the presence of  $\partial\epsilon/\partial T$  terms in the thermodynamic theory, where  $\epsilon$  is the dielectric constant. We neglect these very small differences.

The light scattering spectrum  $I(\omega)$ , which reflects fluctuations in the local dielectric tensor of a fluid, is<sup>(2B),5</sup>

$$I(\omega) \propto 2 \operatorname{Re} \int_0^{\infty} \langle \hat{\alpha}(\mathbf{k}, t) \hat{\alpha}(-\mathbf{k}, 0) \rangle e^{i\omega t} dt \quad (1)$$

where  $\hat{\alpha}(\mathbf{k}, t)$  is the Fourier transform of the polarizability density tensor  $\alpha(\mathbf{R}, t)$ , where  $\mathbf{R}$  is a space point. We can write  $\hat{\alpha}(\mathbf{k}, t)$  as

$$\alpha(\mathbf{k}, t) = \sum_j \alpha_j(t) \exp[i\mathbf{k} \cdot \mathbf{q}_j(t)] \quad (2)$$

$\alpha_j(t)$  is the polarizability tensor of the  $j$ th molecule and  $q_j$  is its translational coordinate, the brackets  $\langle \rangle$  indicate an equilibrium ensemble average, the sum is over all molecules, and the bracketed quantity is an autocorrelation function. For molecules with isotropic polarizabilities, we assume that  $\alpha_j(t)$  is a constant independent of time and independent of molecular position, velocity, and energy; actually intermolecular interactions give rise to both time and temperature dependences but the temperature dependence is probably small (cf. footnote 4 concerning small values of  $\partial\epsilon/\partial T$ ); the time dependence arising from intermolecular pair "collisions" is probably characterized by frequencies much higher than those studied here. The VV or polarized spectrum of a fluid composed of two species (A and B) with isotropic molecular polarizabilities  $\alpha^{(A)}$  and  $\alpha^{(B)}$ , respectively, is thus

$$I(\omega) \propto \operatorname{Re} [\alpha^2 \langle N(\mathbf{k}, \omega) N(-\mathbf{k}, 0) \rangle + \alpha \Delta\alpha \{ N(\mathbf{k}, \omega) \Delta N(\mathbf{k}, 0) + \langle \Delta N(\mathbf{k}, \omega) N(\mathbf{k}, 0) \rangle \} + \Delta\alpha^2 \langle \Delta N(\mathbf{k}, \omega) \Delta N(-\mathbf{k}, 0) \rangle] \quad (3)$$

where

$$\langle N(\mathbf{k}, \omega) N(-\mathbf{k}) \rangle = \int e^{i\omega t} dt \langle N(\mathbf{k}, t) N(-\mathbf{k}, 0) \rangle \quad (4)$$

$$\alpha = \frac{1}{2} [\alpha^{(A)} + \alpha^{(B)}] \quad (5)$$

$$\Delta\alpha = \frac{1}{2} [\alpha^{(A)} - \alpha^{(B)}] \quad (6)$$

$N(\mathbf{k}, t)$  is the transform of the fluctuation  $\delta n(\mathbf{R}, t)$  in the total number density,

$$\delta n(\mathbf{R}, t) = \delta n^{(A)}(\mathbf{R}, t) + \delta n^{(B)}(\mathbf{R}, t) \quad (7)$$

$\Delta N(\mathbf{k}, t)$  is the transform of the fluctuation in the concentration density,

$$\Delta N(\mathbf{k}, t) = [N^{(A)}(\mathbf{k}, t) - N^{(B)}(\mathbf{k}, t)] \quad (8)$$

$N^{(A)}(\mathbf{k}, t)$  is the Fourier transform of  $\delta n^{(A)}(\mathbf{R}, t)$ , the number density fluctuation of the A-th species,

$$\delta n^{(A)}(\mathbf{R}, t) = n^{(A)}(\mathbf{R}, t) - \langle n^{(A)}(\mathbf{R}) \rangle \quad (9)$$

<sup>5</sup>  $I(\omega)$  is also proportional to the local electric field intensity and we neglect the fluctuations in this intensity.

and  $n^{(A)}(\mathbf{R}, t)$  is the instantaneous number density of species A at point  $\mathbf{R}$  in the sample. The number density  $n^{(A)}(\mathbf{R}, t)$  is given by

$$n^{(A)}(\mathbf{R}, t) = \sum_j \delta(\mathbf{R} - \mathbf{q}_j(t)) \Delta_j^{(A)}(t) \quad (10)$$

where  $\Delta_j^{(A)}$  is 1 if  $j$  is an A-type molecule and 0 if it is a B-type molecule; a completely analogous expression holds for  $n^{(B)}(\mathbf{R}, t)$ . If we combine Eqs. (9) and (10), we see that

$$N^{(A)}(\mathbf{k}, t) = \int n^{(A)}(\mathbf{R}, t) [\exp(i\mathbf{k} \cdot \mathbf{R})] d\mathbf{R} - (2\pi)^3 \delta(\mathbf{k}) \frac{N^{(A)}}{V} \quad (11)$$

where  $d\mathbf{R}$  indicates a spatial volume element,  $N^{(A)}$  is the total number of particles of species A, and  $V$  is the volume of the sample. Throughout this work we will *exclude the case of*  $\mathbf{k} \equiv 0$ ; consequently, we can henceforth neglect the term containing  $\delta(\mathbf{k})$  in Eq. (11). It can also be seen that because  $\delta n^{(A)}(\mathbf{R}, t)$  is a fluctuation variable,

$$\langle N(\mathbf{k}, \omega) \rangle = \langle \Delta N(\mathbf{k}, \omega) \rangle = 0 \quad (12)$$

Since we exclude the case  $k = 0$ , we allow  $N^{(A)}$ ,  $N^{(B)}$ ,  $N$ , and  $\Delta N$  to represent total numbers whereas  $N^{(A)}(k)$ ,  $N^{(B)}(k)$ ,  $N(k)$ , and  $\Delta N(k)$  represent Fourier transforms of density fluctuations.

Equation (3) is the fundamental expression which we wish to evaluate. In order to do this, we must calculate the correlation functions in Eq. (3), which involve  $N(k)$  and  $\Delta N(k)$ , the Fourier transforms of the number density and the concentration fluctuation, respectively. Consequently,  $N(k)$  and  $\Delta N(k)$  are the two fundamental or *primary variables*,<sup>(2B)</sup> the variables that enter directly into the expression for  $I(\omega)$ . In addition, we must also consider other variables, which we call *secondary variables*.<sup>(2B)</sup> The secondary variables are needed to describe the time dependence of the primary variables. Since the primary variables are slowly varying quantities, i.e., conserved quantities in the absence of chemical reactions, we must include all other "slow variables" which can in some way affect the long-time evolution of the primary variables. The two conserved quantities  $-i\mathbf{k} \cdot M\mathbf{U}(\mathbf{k})$  and  $E(\mathbf{k})$ , the Fourier transforms of the divergence of the momentum density and of the energy density fluctuation, respectively, are the other relevant slow variables<sup>(3,4,2B)</sup>

$$-i\mathbf{k} \cdot M\mathbf{U}(\mathbf{k}) = -i\mathbf{k} \cdot \sum_j \mathbf{p}_j \exp(i\mathbf{k} \cdot \mathbf{q}_j) \quad (13)$$

$$E(\mathbf{k}) = \sum_j \left[ (p_j^2/2m) + \frac{1}{2} \sum_{j'} U_{jj'} + \varepsilon_j \right] \exp(i\mathbf{k} \cdot \mathbf{q}_j) \quad (14)$$

$M$  is the mass of the sample;  $\mathbf{p}_j$  is the momentum and  $\varepsilon_j$  the internal energy, respectively, of the  $j$ th particle;  $U_{jj'}$  is the intermolecular pair potential;  $k \neq 0$ ; and  $(\mathbf{p}_j, \mathbf{q}_j, \varepsilon_j)$  are all time dependent. We will assume that the four

variables  $\{N(\mathbf{k}), \Delta N(\mathbf{k}), -i\mathbf{k} \cdot M\mathbf{U}(\mathbf{k}), E(\mathbf{k})\}$  constitute a "complete set" of slowly varying quantities in the Hilbert subspace described by Mori.<sup>(29)</sup>  $E(\mathbf{k})$  represents fluctuations in the energy but we allow  $E$  to represent the total energy;  $\mathbf{U}(\mathbf{k})$  represents fluctuations in the flow speed.

The quantities  $\Delta_j^{(A)}$  and  $\varepsilon_j$  require further comment. We consider the complete description of the system in a phase space which consists of the positions ( $\mathbf{q}_j$ ) and translational momenta ( $\mathbf{p}_j$ ) of the center of masses of the particles, and of their relevant internal positions ( $\xi_j$ ) and momenta ( $\pi_j$ ). The internal energy  $\varepsilon_j$  is a function of  $\xi_j$  and  $\pi_j$ , and the intermolecular potential energy  $U$  is not only a function of  $\mathbf{q}_{jj'}$ , where  $\mathbf{q}_{jj'} = \mathbf{q}_j - \mathbf{q}_{j'}$ , but also of  $\xi_j$  and  $\xi_{j'}$ . We shall assume that  $\xi_j$  is a "reaction" coordinate and that for  $\xi_j \leq \xi_0$  the  $j$ th molecule is of species A, i.e.,  $\Delta_j^{(A)} = 1$ ,  $\Delta_j^{(B)} = 0$ ,  $\varepsilon_j = \varepsilon^A$ ; similarly, if  $\xi_j \geq \xi_0$ , then the  $j$ th molecule is of species B, i.e.,  $\Delta_j^{(B)} = 1$ ,  $\Delta_j^{(A)} = 0$ ,  $\varepsilon_j = \varepsilon^B$ . This is a two-site jump model; its application to chemical reactions is obvious, but it can also be used to study rotational and vibrational relaxation.

We are interested in obtaining equations of motion for the quantities  $N(\mathbf{k}), \Delta N(\mathbf{k}), E(\mathbf{k}), -i\mathbf{k} \cdot M\mathbf{U}(\mathbf{k})$ . In order to obtain these equations, we must evaluate the various relevant time derivatives. In particular,

$$\dot{N}(\mathbf{k}, t) = i\mathbf{k} \cdot M\mathbf{U}(\mathbf{k}, t)/m \quad (15)$$

where we have chosen both species with the same molecular mass  $m$ . Furthermore, for short-range intermolecular interactions, in the limit of small  $k$ ,

$$-i\mathbf{k} \cdot M\mathbf{U}(\mathbf{k}, t) = k^2 \sigma_{kk} \quad (16)$$

where  $\sigma_{\alpha\beta}$  is the microscopic stress tensor defined as

$$\sigma_{\alpha\beta}(\mathbf{k}, t) = \sum_j \frac{d}{dt} [p_{\alpha j}(t) q_{\beta j}(t)] \exp[i\mathbf{k} \cdot \mathbf{q}_j(t)] \quad (17)$$

The subscripts  $\alpha$  and  $\beta$  indicate laboratory axes, and  $\sigma_{kk}$  indicates  $\sigma_{zz}$  if  $\mathbf{k}$  is along  $z$ . Slightly more complicated is the derivative of  $\Delta N(\mathbf{k})$ :

$$\begin{aligned} \Delta \dot{N}(\mathbf{k}, t) &= (d/dt) \sum [\Delta_j^{(A)}(\xi_j(t)) - \Delta_j^{(B)}(\xi_j(t))] \\ &\quad \times \exp[i\mathbf{k} \cdot \mathbf{q}_j(t)] \end{aligned} \quad (18)$$

In the limit of small  $k$ , this quantity can be rewritten, provided the molecular interactions are short range, as

$$\Delta \dot{N}(\mathbf{k}, t) = i\mathbf{k} \cdot \boldsymbol{\sigma}^{(\Delta n)}(\mathbf{k}, t) + \gamma(\mathbf{k}, t) \quad (19)$$

where

$$\gamma(\mathbf{k}, t) = \sum_j \dot{\xi}_j(t) 2\delta(\xi_j(t) - \xi_0) \exp[i\mathbf{k} \cdot \mathbf{q}_j(t)] \quad (20)$$

$$\boldsymbol{\sigma}^{(\Delta n)}(\mathbf{k}, t) = \sum_j \dot{q}_j [\Delta_j^{(A)}(\xi_j(t)) - \Delta_j^{(B)}(\xi_j(t))] \exp[i\mathbf{k} \cdot \mathbf{q}_j(t)] \quad (21)$$

and  $\delta$  is a delta function. Whereas  $N(\mathbf{k})$  and  $-i\mathbf{k}M \cdot \mathbf{U}(\mathbf{k})$  are conserved [i.e.,  $\dot{N}(\mathbf{k})$  and  $\mathbf{U}(\mathbf{k}) \rightarrow 0$  as  $k \rightarrow 0$ ],  $\Delta N$  is conserved only if  $\dot{\xi}_j(t) = 0$ , i.e., if  $\gamma = 0$ , which is the situation for a nonreacting binary fluid. Finally, since  $E(\mathbf{k})$  is a conserved quantity,

$$\dot{E}(\mathbf{k}, t) = i\mathbf{k} \cdot \boldsymbol{\sigma}^{(e)}(\mathbf{k}, t) \quad (22)$$

where the energy flux density  $\boldsymbol{\sigma}^{(e)}$  is, in the low- $k$  limit,

$$\begin{aligned} \boldsymbol{\sigma}^{(e)}(\mathbf{k}, t) = \sum_j \left\{ \dot{\mathbf{q}}_j \left[ \frac{p_j^2}{2m} + \left( \frac{1}{2} \sum_{j'} U_{jj'} \right) + \varepsilon_j \right] \right. \\ \left. + \frac{1}{4} \sum_{j' \neq j} \mathbf{q}_{j'} (\dot{\mathbf{q}}_j + \dot{\mathbf{q}}_{j'}) \cdot \nabla_j U_{jj'} \right. \\ \left. + \frac{1}{4} \sum_{j' \neq j} \mathbf{q}_{j'} (\dot{\xi}_{j'} - \dot{\xi}_j) \frac{\partial U_{jj'}}{\partial \xi_j} \right\} \exp(i\mathbf{k} \cdot \mathbf{q}_j) \quad (23) \end{aligned}$$

This expression is derived in Appendix A. The presence of  $\varepsilon_j$  in  $\boldsymbol{\sigma}^{(e)}$  is a consequence of the internal motions; the last term arises because the potential energy of a molecule changes as either it or its neighbors convert from one species to the other.

It can readily be shown<sup>(3,29)</sup> that all the quantities of interest, in the theory to be discussed below, are dependent only upon the magnitude of  $\mathbf{k}$ ; we shall therefore introduce a scalar notation in which  $N(k, t)$  replaces  $N(\mathbf{k}, t)$ , and similar replacements are made for the other variables.<sup>6</sup>

### 3. THEORY: MORI FORMULATION OF TRANSPORT THEORY

Now we wish to use Mori's theory<sup>(29)</sup> to obtain the correlation functions in Eq. (3). To do so we introduce a vector  $\mathcal{A}$  in Hilbert space, where the components of  $\mathcal{A}$  are the dynamical variables described in the last section:

$$\mathcal{A}(k, t) = \{N(k, t), \Delta N(k, t), E(k, t), -i\mathbf{k} \cdot M\mathbf{U}(k, t)\} \quad (24)$$

In the Mori linear response theory the matrix of the transforms of correlation functions  $\langle \mathcal{A}(\omega) \mathcal{A}^* \rangle$  are given by the expression

$$\langle \mathcal{A}(\omega) \mathcal{A}^* \rangle = [i\omega 1 - i\Omega + K(\omega)]^{-1} \langle \mathcal{A} \mathcal{A}^* \rangle \quad (25)$$

where  $\langle \mathcal{A}(\omega) \mathcal{A}^* \rangle$  is the half-Fourier time transform of the correlation function  $\langle \mathcal{A}(t) \mathcal{A}^* \rangle$ ,

$$i\Omega = \langle \dot{\mathcal{A}} \mathcal{A}^* \rangle \langle \mathcal{A} \mathcal{A}^* \rangle^{-1} \quad (26)$$

$$K(\omega) = \langle \dot{\mathcal{A}}^+(\omega) (\dot{\mathcal{A}}^+)^* \rangle \langle \mathcal{A} \mathcal{A}^* \rangle^{-1} \quad (27)$$

<sup>6</sup>  $\Delta N$  is often called a progress variable and is relabeled  $\xi$ .



$\langle \dot{A}^+(\omega)(\dot{A}^+)^* \rangle$  is the half-Fourier time transform of  $\langle \dot{A}^+(t)(\dot{A}^+)^* \rangle$ ,

$$\dot{A}^+(t) = \{\exp[i(1 - P)Lt]\}i(1 - P)LA \tag{28}$$

$iL$  is the ordinary Liouville operator, and the projection operator  $P$  acting on an arbitrary vector  $G$  yields

$$PG = \langle GA^* \rangle \langle AA^* \rangle^{-1} A \tag{29}$$

If on the long time scale of interest, the four variables  $\{N(k), \Delta N(k), E(k), -ik \cdot MU(k)\}$  form a complete set, then at low frequency  $\omega$ , the transport matrix  $K(\omega)$  is independent of  $\omega$ . We will assume that these four variables do indeed form a complete set; this is our fundamental assumption.

The coupled transport equations in Eq. (25), together with a transport matrix  $K(\omega)$  that is independent of  $\omega$ , are valid only at small  $\omega$ . We take

$$\langle A \rangle = 0 \tag{30}$$

i.e.,  $A$  is a fluctuation of a quantity  $\mathcal{A}$  from its equilibrium value. Thus  $A$  is always chosen so that

$$A = \mathcal{A} - \langle \mathcal{A} \rangle \tag{31}$$

This is true of the variables in Eq. (24).

It is important to explain why we work with transformed quantities such as  $N(\mathbf{k}, t)$  rather than fluctuations such as  $\delta n(\mathbf{R}, t)$ . First of all, it is  $N(\mathbf{k}, t)$  and not  $\delta n(\mathbf{R}, t)$  that enters as a primary variable in the expression for the spectrum in Eq. (3). Second, in the transport equations given in Eq. (25), the vector  $\mathbf{A}$  in configuration space must include elements at each position, e.g.,  $A(\mathbf{R}, t), A(\mathbf{R}', t), A(\mathbf{R}'', t), \dots$ ; thus Eq. (25) would have to represent an infinite set of coupled differential equations or, in continuum notation, a finite set of integrodifferential equations.<sup>(29)</sup> This complication arises because terms of the form  $\langle A(\mathbf{R}, 0)A(\mathbf{R}', 0) \rangle$  with  $\mathbf{R} \neq \mathbf{R}'$  do not necessarily vanish. However, in reciprocal or lattice space, all these problems vanish since terms of the form  $\langle A(\mathbf{k}, 0)A^*(\mathbf{k}', 0) \rangle$  vanish, because of translational invariance,<sup>(29)</sup> i.e.,

$$\langle A(\mathbf{k}, 0)A^*(\mathbf{k}', 0) \rangle = \langle A(\mathbf{k}, 0)A(\mathbf{k}', 0) \rangle V^{-1} \delta(\mathbf{k} - \mathbf{k}') \tag{32}$$

where  $V$  is the volume of the sample.

#### 4. THEORY: THERMODYNAMIC EQUIVALENCE OF TIME-INDEPENDENT CORRELATION FUNCTIONS

Mori<sup>(29,32)</sup> has developed a procedure for relating the matrix elements of the time-independent equilibrium matrices  $\langle AA^* \rangle$  and  $\langle \dot{A}A^* \rangle$  to thermo-

dynamic quantities, and we discuss a simple variant of his procedure. The results of this treatment can be presented as follows. In the linear response limit, the distribution function  $\rho$  for a grand canonical ensemble can be expressed as

$$\rho = \rho_0 [1 + \mathcal{A}(\mathbf{R}) \delta \mathbf{B}(\mathbf{R})] \quad (33)$$

where  $\rho_0$  represents the equilibrium ensemble in the absence of any external disturbances, and  $\rho$  represents the ensemble at local equilibrium in the presence of small external perturbations  $\delta \mathbf{B}(\mathbf{R})$  conjugate to the  $\mathcal{A}(\mathbf{R})$ 's. With the aid of this distribution function, one can readily show that

$$\overline{A(k)} = [1/(2\pi)^3 k_B T V] \langle A(k) A^*(k) \rangle \cdot \mathbf{B}(k) \quad (34)$$

where the bar over  $\overline{A(k)}$  represents the average value of  $A(k)$  in the perturbed ensemble,  $\langle \rangle$  indicates an average in the unperturbed ensemble,  $\mathbf{B}(k)$  is the transform of  $\delta \mathbf{B}(\mathbf{R})$ , and  $A(k)$  is the transform of  $\mathcal{A}(\mathbf{R})$ . Since  $k \neq 0$ ,  $A(k)$  is actually the transform of the fluctuation  $[\mathcal{A}(\mathbf{R}) - \langle \mathcal{A} \rangle]$  [See eqs. (10), (11), (30), and (31)]. Our variables are

$$A(k) = \begin{pmatrix} N(k) \\ \Delta N(k) \\ E(k) \\ -i\mathbf{k} \cdot M\mathbf{U}(k) \end{pmatrix} \quad (35)$$

where

$$N(k) = N^{(A)}(k) + N^{(B)}(k) \quad (36)$$

and the other variables are defined in Eqs. (8), (13), and (14). We note that  $N(k)$  is a number fluctuation and  $N$  is the total number of particles;  $\overline{N(k)}$  and  $N$  are very different. However, derivatives of  $\overline{N(k)}$  and of  $N$  are identical, so that we may replace  $N(k)$  by  $N$  in all derivatives. The same holds for the pairs  $\{\overline{\Delta N(k)}, \Delta N\}$  and  $\{\overline{E(k)}, E\}$ , where  $E$  is the total energy. The transforms of the conjugate perturbing forces  $\delta \mathbf{B}(\mathbf{R})$ , are, in the low- $k$  limit,

$$\mathbf{B}(k) = (2\pi)^3 V \begin{pmatrix} \frac{1}{2} T \delta\{\mu(k)/T(k)\} \\ \frac{1}{2} T \delta\{\Delta\mu(k)/T(k)\} \\ T \delta\{1/T(k)\} \\ \overline{U(k)}/ik \end{pmatrix} \quad (37)$$

where  $\mu$  and  $\Delta\mu$  are chemical potentials defined as<sup>7</sup>

$$\mu = \mu_A + \mu_B \quad (38)$$

$$\Delta\mu = \mu_A - \mu_B \quad (39)$$

<sup>7</sup>  $-\Delta\mu$  is often called the chemical affinity and is represented by  $-A$ .

where  $\mu_A$  and  $\mu_B$  are the chemical potentials (per molecule) of species A and B, respectively, and  $\overline{U(k)}$  is the fluctuation in the mean flow speed. A rather complete derivation of the above results is given in Appendix B. [See Eq. (B-9) for a precise definition of  $\delta$  in the low  $k$ -limit.]

If the elements of  $\overline{A(k)}$  and  $B(k)$  are represented as  $\overline{A_a(k)}$  and  $B_b(k)$ , respectively, then from Eq. (34) we obtain

$$(2\pi)^3 \left( \frac{\partial \overline{A_a(k)}}{\partial B_b(k)} \right)_{B_c(k)} = (k_B TV)^{-1} \langle A(k) A^*(k) \rangle_{ab} \quad (40)$$

$$\frac{1}{(2\pi)^3} \left( \frac{\partial B_a(k)}{\partial \overline{A_b(k)}} \right)_{\overline{A_c(k)}} = (k_B TV) [\langle A(k) A^*(k) \rangle^{-1}]_{ab} \quad (41)$$

where  $\overline{A_c(k)}$  and  $B_c(k)$  represent all components of  $\overline{A(k)}$  and  $B(k)$ , respectively, except  $\overline{A_b(k)}$  and  $B_b(k)$ . The volume  $V$  is also held constant; this is equivalent to working at a fixed  $k$ . These results are valid if only terms linear in  $B(k)$  are retained in  $\overline{A(k)}$ ; therefore the derivatives are taken in the limit of small  $B(k)$ . In this limit, the system is homogeneous and the only Fourier components present are those for which  $k$  is small. We thus have the following interpretation of the above results: The brackets  $\langle \rangle$  indicate equilibrium at unconstrained equilibrium [ $B(k=0) = 0$ ]; the quantities  $\overline{A(k \rightarrow 0)}$  are thermodynamic or mean fluctuations from equilibrium; and the “forces”  $B(k \rightarrow 0)$  are thermodynamic potentials conjugate to the  $\overline{A(k \rightarrow 0)}$ ’s; the fluctuations vanish at equilibrium, i.e.,  $\overline{A(k=0)} = \langle A(k=0) \rangle = 0$  at  $B(k=0) = 0$ ; but if  $k \neq 0$  and  $B(k) \neq 0$ , we can have an equilibrium constrained by the “forces”  $B(k)$ , and in this case  $\overline{A(k)} \neq 0$ . The correlation functions  $\langle A(k) A^*(k) \rangle$  are mean square fluctuations of thermodynamic quantities at unconstrained equilibrium.

## 5. EVALUATION OF $\langle AA \rangle^{-1}$ MATRIX

In terms of our variables  $\{N(k), \Delta N(k), E(k), -i\mathbf{k} \cdot M\mathbf{U}(k)\}$  the  $\langle AA^* \rangle$  matrix introduced above becomes

$$\langle A(k) A^*(k) \rangle = \begin{pmatrix} \langle N(k) N^*(k) \rangle & \langle N(k) \Delta N^*(k) \rangle & \langle N(k) E^*(k) \rangle & 0 \\ \langle \Delta N(k) N^*(k) \rangle & \langle \Delta N(k) \Delta N^*(k) \rangle & \langle \Delta N(k) E^*(k) \rangle & 0 \\ \langle E(k) N^*(k) \rangle & \langle E(k) \Delta N^*(k) \rangle & \langle E(k) E^*(k) \rangle & 0 \\ 0 & 0 & 0 & k^2 M^2 \langle U(k) U^*(k) \rangle \end{pmatrix} \quad (42)$$

There is no coupling between  $\{N(k), \Delta N(k), E(k)\}$  and  $\{-i\mathbf{k} \cdot M\mathbf{U}(k)\}$  because the connecting matrix elements all involve averages of expressions that are linear in the momentum. In the limit  $k \rightarrow 0$ , all the matrix elements in Eq. (42)

are equilibrium quantities and therefore directly related to thermodynamic quantities. By means of thermodynamic fluctuation theory, as outlined in the last section, in the low- $k$  limit we can readily evaluate the elements of the inverse matrix  $\langle A(k)A^*(k) \rangle^{-1}$ . We make use of Eq. (42) and the identifications in Eqs. (35), (37), (40), and (41) to obtain

$$\lim_{k \rightarrow 0} \langle A(k)A^*(k) \rangle^{-1} = \frac{1}{k_B T} \begin{pmatrix} \frac{T}{2} \left( \frac{\partial \mu / T}{\partial N} \right)_{\Delta N, E, V} & \frac{T}{2} \left( \frac{\partial \mu / T}{\partial \Delta N} \right)_{N, E, V} & \frac{T}{2} \left( \frac{\partial \mu / T}{\partial E} \right)_{N, \Delta N, V} & 0 \\ \frac{T}{2} \left( \frac{\partial \Delta \mu / T}{\partial N} \right)_{\Delta N, E, V} & \frac{T}{2} \left( \frac{\partial \Delta \mu / T}{\partial \Delta N} \right)_{N, E, V} & \frac{T}{2} \left( \frac{\partial \Delta \mu / T}{\partial E} \right)_{N, \Delta N, V} & 0 \\ \frac{1}{T} \left( \frac{\partial T}{\partial N} \right)_{\Delta N, E, V} & \frac{1}{T} \left( \frac{\partial T}{\partial \Delta N} \right)_{N, E, V} & \frac{1}{T} \left( \frac{\partial T}{\partial E} \right)_{N, \Delta N, V} & 0 \\ 0 & 0 & 0 & \frac{1}{k^2 M} \end{pmatrix} \quad (43)$$

We have replaced  $\overline{N(k)}$ ,  $\overline{\Delta N(k)}$ , and  $\overline{E(k)}$  by  $N$ ,  $\Delta N$ , and  $E$  as explained above.  $V$  is held constant because we are working at constant  $k$ . In all these thermodynamic derivatives,  $\overline{U} = 0$ , which means that the total and internal energies are equivalent.

We see that  $\langle A(k)A^*(k) \rangle$  and  $\langle A(k)A^*(k) \rangle^{-1}$  are both Hermitian. From Eq. (43) we can therefore obtain the interrelationships

$$\left( \frac{\partial \Delta \mu / T}{\partial N} \right)_{\Delta N, E, V} = \left( \frac{\partial \mu / T}{\partial \Delta N} \right)_{N, E, V} \quad (44a)$$

$$\frac{1}{T} \left( \frac{\partial T}{\partial N} \right)_{\Delta N, E, V} = \frac{T}{2} \left( \frac{\partial \mu / T}{\partial E} \right)_{N, \Delta N, V} \quad (44b)$$

$$\frac{2}{T} \left( \frac{\partial T}{\partial \Delta N} \right)_{N, E, V} = T \left( \frac{\partial \Delta \mu / T}{\partial E} \right)_{N, \Delta N, V} \quad (44c)$$

## 6. EVALUATION OF THE $i\Omega$ MATRIX

Next we wish to evaluate the matrix  $i\Omega$  in the Langevin equation derived by Mori, i.e., Eqs. (25) and (26). To do this, we note that in the linear response region, the expression

$$\overline{\dot{A}(k)} = (2\pi^3 k_B T V)^{-1} \langle \dot{A}(k)A^*(k) \rangle \cdot B(k) \quad (45)$$

can be obtained in exactly the same manner by which Eq. (34) was derived. If we now combine this expression with Eq. (34), we obtain

$$\overline{\dot{A}(k)} = \langle \dot{A}(k)A^*(k) \rangle \langle A(k)A^*(k) \rangle^{-1} \cdot \overline{A(k)} \quad (46)$$

and by differentiating and comparing with Eq. (26), we obtain

$$i\Omega_{ab} = \left( \frac{\partial \overline{A_a(k)}}{\partial A_b(k)} \right)_{\overline{A_c(k)}} \quad (47)$$

(See the discussion in Section 4.) It can readily be seen that the only non-vanishing elements of  $\Omega_{ab}$  are those that connect  $-ikMU(k)$  with  $N(k)$ ,  $\Delta N(k)$ , and  $E(k)$ . If we make use of Eq. (47) together with the identifications in Eqs. (35) and (37), we obtain

$$\lim_{k \rightarrow 0} i\Omega = \begin{pmatrix} 0 & 0 & 0 & \frac{1}{kM} \left( \frac{\partial \dot{N}}{\partial U} \right)_{N, \Delta N, E, V} \\ 0 & 0 & 0 & \frac{1}{kM} \left( \frac{\partial \Delta \dot{N}}{\partial U} \right)_{N, \Delta N, E, V} \\ 0 & 0 & 0 & \frac{1}{kM} \left( \frac{\partial \dot{E}}{\partial U} \right)_{N, \Delta N, E, V} \\ -kM \left( \frac{\partial \dot{U}}{\partial N} \right)_{\Delta N, E, U, V} & -kM \left( \frac{\partial \dot{U}}{\partial \Delta N} \right)_{N, E, U, V} & -kM \left( \frac{\partial \dot{U}}{\partial E} \right)_{N, \Delta N, U, V} & 0 \end{pmatrix} \quad (48)$$

In the thermodynamic relationships we have replaced  $\lim_{k \rightarrow 0} \overline{U(k)}$  by  $U$ .

We can next evaluate the various time derivatives appearing in Eq. (48) in terms of thermodynamic quantities. From Eqs. (15) and (16), together with Eq. (38), we obtain

$$\dot{N} = ik(M/m)U \quad (49)$$

where  $M$  is the sample mass and  $m$  the molecular mass, and in the low- $k$  limit

$$\overline{A_a(k)} = -ikM\dot{U} = k^2 p V \quad (50)$$

where the pressure  $p$  is defined as

$$Vp = \bar{\sigma}_{kk} \quad (51)$$

If we go back to Eq. (26) and compare it with Eq. (48), we see that

$$\begin{aligned} \partial \Delta \dot{N} / \partial U &= \langle U(k)U(k)^* \rangle^{-1} \langle \Delta \dot{N}(k)U(k)^* \rangle \\ &= -\langle U(k)U(k)^* \rangle^{-1} \langle \dot{U}(k) \Delta N^*(k) \rangle^* \end{aligned} \quad (52a)$$

$$\begin{aligned} \partial \dot{E} / \partial U &= \langle U(k)U(k)^* \rangle^{-1} \langle \dot{E}(k)U^*(k) \rangle \\ &= -\langle U(k)U(k)^* \rangle^{-1} \langle \dot{U}(k)E(k)^* \rangle^* \end{aligned} \quad (52b)$$

From Eq. (45) we see that

$$\left(\frac{\partial \dot{U}}{\partial B_{\Delta N}}\right)_{B_N, B_E, B_U} = \langle \dot{U}(k) \Delta N^*(k) \rangle \frac{1}{k_B T V} \quad (53a)$$

$$\left(\frac{\partial \dot{U}}{\partial B_E}\right)_{B_N, B_{\Delta N}, B_U} = \langle \dot{U}(k) E^*(k) \rangle \frac{1}{k_B T V} \quad (53b)$$

We now combine Eqs. (52a), (53a), and (50):

$$\frac{iM}{k} \frac{\partial \Delta \dot{N}}{\partial U} = \frac{-k_B T V^2}{\langle U(k) U^*(k) \rangle} \left(\frac{\partial p}{\partial B_{\Delta N}}\right)_{B_N, B_E, B_U, V} \quad (54a)$$

Similarly, we can combine Eqs. (52b), (53b), and (50):

$$\frac{iM}{k} \frac{\partial \dot{E}}{\partial U} = \frac{-k_B T V^2}{\langle U(k) U^*(k) \rangle} \left(\frac{\partial p}{\partial B_E}\right)_{B_N, B_{\Delta N}, B_U, V} \quad (54b)$$

Finally, we substitute Eqs. (54ab), (50), (37), and the relation

$$M \langle U(k) U^*(k) \rangle = k_B T \quad (55)$$

into the expression for  $\Omega$  in Eq. (48):

$$\lim_{k \rightarrow 0} i\bar{\Omega} = V \begin{pmatrix} 0 & 0 & 0 & -\frac{1}{mV} \\ 0 & 0 & 0 & -\frac{2}{mN} \left(\frac{\partial p}{\partial \Delta \mu}\right)_{\mu, T, V} \\ 0 & 0 & 0 & -\frac{T}{mN} \left(\frac{\partial p}{\partial T}\right)_{\mu/T, \Delta \mu/T, V} \\ k^2 \left(\frac{\partial p}{\partial N}\right)_{\Delta N, E, V} & k^2 \left(\frac{\partial p}{\partial \Delta N}\right)_{N, E, V} & k^2 \left(\frac{\partial p}{\partial E}\right)_{N, \Delta N, V} & 0 \end{pmatrix} \quad (56)$$

Note again that all derivatives are taken with  $U = 0$ , and that  $\mu$  and  $\Delta \mu$  are chemical potentials per molecule.

## 7. TRANSPORT COEFFICIENTS

Finally we turn to the evaluation of the transport coefficients  $K(\omega)$  in Eq. (27). In evaluating the  $\langle (\dot{A}^+) \dot{A}^{+*}(t) \rangle$  matrix, we can see immediately that many terms vanish. First of all

$$\dot{N}^+(\mathbf{k}, t) \equiv 0 \quad (57)$$

Second, for isotropic systems,

$$\langle \dot{A}^+(t) (\dot{U}^+)^* \rangle = \langle \dot{U}^+(t) (\dot{A}^+)^* \rangle \equiv 0 \quad (58)$$

for  $A \neq -ikUM$ ; this can be proved by noting that for all times,  $-ikMU^+$  has even parity in the spatial coordinate and  $\dot{A}^+$  has odd parity in either

spatial or internal ( $\xi$ ) coordinates. Thus all elements of  $\langle \dot{A}^+(\omega) \dot{A}^{+*} \rangle$  vanish except

$$\langle \dot{U}^+(\omega) \dot{U}^{+*} \rangle = \langle \sigma_{kk}^+(\omega) \sigma_{kk}^{+*} \rangle = k_B T V \left( \frac{4}{3} \eta + \eta_v \right) \quad (59)$$

$$\langle \dot{E}^+(\omega) \dot{E}^{+*} \rangle = k^2 \langle \sigma_k^{(e)+}(\omega) \sigma_k^{(e)+*} \rangle = k^2 k_B T^2 V \kappa \quad (60)$$

$$\langle \Delta \dot{N}^+(\omega) \Delta \dot{N}^{+*} \rangle = k^2 \langle \sigma_k^{(\Delta n)+}(\omega) \sigma_k^{(\Delta n)+*} \rangle + \langle \gamma^+(\omega) \gamma^{+*} \rangle = [k^2 D + R] N \quad (61)$$

$$\langle \Delta \dot{N}^+(\omega) \dot{E}^{+*} \rangle = \langle \dot{E}^{+*}(\omega) \Delta \dot{N}^{+*} \rangle^* = k^2 \langle \sigma_k^{(e)+}(\omega) \sigma_k^{(\Delta n)+*} \rangle = k^2 D_T V \quad (62)$$

where the various coefficients  $\eta$ ,  $\eta_v$ ,  $\kappa$ ,  $D$ , and  $D_T$  are defined by these equations and are the coefficients of shear viscosity, bulk viscosity, thermal conductivity, appropriate diffusion, and appropriate thermal diffusion, respectively, and  $R$  is the "reaction" decay constant. In the low- $\omega$  limit, the limit in which we are interested, the transport coefficients are all real. We can now combine Eqs. (59)–(62) with Eqs. (41) and (44) to obtain the transport matrix  $K = \lim_{\omega \rightarrow 0} K(\omega)$ :

$K =$

$$\begin{pmatrix} 0 & 0 & 0 & 0 \\ (Dk^2 + R) \frac{N}{2k_B} & (Dk^2 + R) \frac{N}{2k_B} & (Dk^2 + R) \frac{N}{k_B T^2} & 0 \\ \times \left( \frac{\partial(\mu/T)}{\partial \Delta N} \right)_{N,E} & \times \left( \frac{\partial \Delta \mu/T}{\partial \Delta N} \right)_{N,E} & \times \left( \frac{\partial T}{\partial \Delta N} \right)_{N,E} & \\ + \frac{k^2 D_T V}{k_B T^2} \left( \frac{\partial T}{\partial N} \right)_{\Delta N,E} & + \frac{k^2 D_T V}{k_B T^2} \left( \frac{\partial T}{\partial \Delta N} \right)_{N,E} & + \frac{k^2 V}{k_B T^2} \left( \frac{\partial T}{\partial E} \right)_{N,\Delta N} & \\ k^2 \left[ \frac{\kappa T^2 V}{2} \right. & k^2 \left[ \frac{T^2 V \kappa}{2} \right. & k^2 \left[ V \kappa \left( \frac{\partial T}{\partial E} \right)_{N,\Delta N} \right. & 0 \\ \times \left( \frac{\partial \mu/T}{\partial E} \right)_{N,\Delta N} & \times \left( \frac{\partial \Delta \mu/T}{\partial E} \right)_{N,\Delta N} & \left. + \frac{D_T V}{2k_B} \left( \frac{\partial \Delta \mu/T}{\partial E} \right)_{N,\Delta N} \right] & \\ \left. + \frac{D_T V}{2k_B} \left( \frac{\partial \Delta \mu/T}{\partial N} \right)_{\Delta N,E} \right] & \left. + \frac{D_T V}{2k_B} \left( \frac{\partial \Delta \mu/T}{\partial \Delta N} \right)_{N,E} \right] & & \\ 0 & 0 & 0 & (k^2/\rho) \left( \frac{4\eta}{3} + \eta_v \right) \end{pmatrix} \quad (63)$$

All the derivatives are taken at constant  $V$  and at  $U = 0$ .

The equations derived above differ slightly from those obtained for systems whose internal dynamics are uncoupled to the hydrodynamic modes.<sup>(3)</sup> First of all, the local energy density and its conjugate potential are modified by the presence of the internal energy of the molecules. Second, the matrix of transport coefficients contains a dissipative decay term  $R$  which is not proportional to  $k^2$ .

## 8. TRANSPORT MATRIX

One finds that  $D_T \ll D$ , and in order to simplify the results, we shall set

$$D_T = 0 \quad (64)$$

This has no appreciable effect on the results, as has been discussed by Mountain and Deutch.<sup>(6)</sup> Additional simplifications occur if we introduce the following effective transport quantities:

$$D' = \frac{DN}{2k_B} \left( \frac{\partial \Delta\mu/T}{\partial \Delta N} \right)_{N,E,V} \quad (65)$$

$$R' = \frac{RN}{2k_B} \left( \frac{\partial \Delta\mu/T}{\partial \Delta N} \right)_{N,E,V} \quad (66)$$

$$\kappa' = \kappa V \left( \frac{\partial T}{\partial E} \right)_{N,\Delta N,V} \quad (67)$$

$$\eta' = \left( \frac{4}{3}\eta + \eta_v \right) / \rho \quad (68)$$

$D'$  is a mutual diffusion constant,  $\eta'$  is an intrinsic total viscosity coefficient, and  $(\partial E/\partial T)_{N,\Delta N,V}$  is the heat capacity at constant volume for a nonreacting solution. If we make use of the approximation in Eq. (64) and the definitions in Eqs. (65)–(68), the transport matrix  $-i\Omega + K$  becomes

$$K - i\Omega = \begin{pmatrix} 0 & 0 & 0 & \frac{1}{m} \\ (D'k^2 + R') & (D'k^2 + R') & \frac{2(D'k^2 + R')}{T^2} & \frac{2V}{TNm} \left( \frac{\partial p}{\partial \Delta\mu/T} \right)_{\mu,T} \\ \times \left( \frac{\partial \mu/T}{\partial \Delta\mu/T} \right)_{N,E} & & \times \left( \frac{\partial T}{\partial \Delta\mu/T} \right)_{N,E} & \\ k^2\kappa' \frac{T^2}{2} \left( \frac{\partial \mu/T}{\partial T} \right)_{N,\Delta N} & \frac{k^2\kappa'T^2}{2} \left( \frac{\partial \Delta\mu/T}{\partial T} \right)_{N,\Delta N} & k^2\kappa' & \frac{VT}{Nm} \left( \frac{\partial p}{\partial T} \right)_{\mu,T,\Delta\mu/T} \\ -Vk^2 \left( \frac{\partial p}{\partial N} \right)_{\Delta N,E} & -Vk^2 \left( \frac{\partial p}{\partial \Delta N} \right)_{N,E} & -Vk^2 \left( \frac{\partial p}{\partial E} \right)_{N,\Delta N} & k^2\eta' \end{pmatrix} \quad (69)$$

Again all derivatives are taken at constant volume  $V$  and at  $U = 0$ . The transport equations associated with this matrix are equivalent to the appropriate equations obtained from irreversible thermodynamics. These equations describe the fluctuations monitored in a light scattering experiment, fluctuations in a given volume element (determined by  $k$ ) at a fixed position in space (determined by the scattering geometry). The connection is proved in Appendix C.

## 9. CALCULATION OF LIGHT SCATTERING SPECTRUM

The expression presented in Eq. (3) for the light scattering spectrum depends upon correlation functions whose time dependence is determined by



the coupled transport equations, Eq. (25), with the transport matrix given by Eq. (69). We can solve these transport equations by inverting the  $4 \times 4$  response matrix  $[i\omega 1 - i\Omega + K]$ . The most convenient way of representing the results is to express the spectrum as a sum of four generalized Lorentzian lines of the form  $L_j(\omega)$ :

$$L_j(\omega) = \frac{\text{Re}(I_j)\Gamma_j}{\Gamma_j^2 + (\omega - \omega_j)^2} + \frac{\text{Im}(I_j)\Gamma_j}{\Gamma_j^2 + (\omega - \omega_j)^2} \quad (70)$$

where  $\Gamma_j$  is the half-width and  $\omega_j$  the position of the line, and  $\text{Re}(I_j)$  and  $\text{Im}(I_j)$  are the intensities of the "normal" and "dispersive" parts, respectively. Such Lorentzian solutions for  $\langle A(\omega)A^* \rangle$  in Eq. (25) can readily be obtained; first one obtains the four roots or eigenvalues  $\lambda_j$  of the secular equation

$$[\lambda_j 1 - i\Omega + K] = 0 \quad (71)$$

As we shall show below, there are two real and two complex eigenvalues  $\lambda_j$  for this secular equation. We can conveniently express the two real ones as

$$\lambda_1 = \Gamma_R \quad (72)$$

$$\lambda_2 = \Gamma_T \quad (73)$$

where the subscripts  $R$  and  $T$  stand for reactive and thermal modes, respectively. The complex solutions can be expressed as

$$\lambda_{\pm} = \Gamma_s \pm ick \quad (74)$$

where the subscript  $s$  stands for sound modes and  $c$ , as we shall see, represents the sound speed. We can then write  $I(\omega)$  in Eq. (3) as

$$I(\omega) = \frac{\Gamma_R I_R}{\Gamma_R^2 + \omega^2} + \frac{\Gamma_T I_T}{\Gamma_T^2 + \omega^2} + \frac{\Gamma_s(\text{Re } I_s) + (\omega - ck)(\text{Im } I_s)}{\Gamma_s + (\omega - ck)^2} + \frac{\Gamma_s(\text{Re } I_s) + (\omega + ck)(\text{Im } I_s)}{\Gamma_s + (\omega + ck)^2} \quad (75)$$

where the intensity factors  $I_j$  are specified by

$$(k_B T)^{-1} I_j = 2 \left\{ \alpha^2 \Phi_j^{(NN)} \left( \frac{\partial N}{\partial \mu} \right)_{\Delta\mu, T, V} + \Delta \alpha^2 \Phi_j^{(\Delta N \Delta N)} \left( \frac{\partial \Delta N}{\partial \mu} \right)_{\mu, T, V} + \alpha \Delta \alpha \left[ \Phi_j^{(N, \Delta N)} \left( \frac{\partial N}{\partial \mu} \right)_{\mu, T, V} + \Phi_j^{(\Delta N, N)} \left( \frac{\partial \Delta N}{\partial \mu} \right)_{\Delta\mu, T, V} \right] \right\} \times \{(-\lambda_j + \lambda_{j'})(-\lambda_j + \lambda_{j''})(-\lambda_j + \lambda_{j'''})\}^{-1} \quad (76)$$

with  $j \neq j' \neq j'' \neq j'''$ , the  $\Phi_j^{(ab)}$  are

$$\Phi_j^{(ab)} = \sum_{a'} \{ \lambda_j 1 - i\Omega + K \}_{aa'} \left( \frac{\partial \overline{A_{a'}}}{\partial B_b} \right)_{B_c B_{c'} B_{c''}} \quad (77)$$

where  $\{\lambda_j 1 - i\Omega + K\}_{aa'}$  is the  $aa'$  cofactor of the matrix  $[\lambda_j 1 - i\Omega + K]$ , and where  $c' \neq c'' \neq c''' \neq b$ . Equation (75) represents the decomposition of the spectrum into four Lorentzians.

It follows from the material above that  $\Phi_R^{(aa')}$  and  $\Phi_T^{(aa')}$  are real but  $\Phi_S^{(aa')}$  is complex.

## 10. EIGENVALUES $\lambda_j$ OF TRANSPORT EQUATIONS

In order to express the spectrum  $I(\omega)$ , we make use of Eq. (75) together with the relations in Eqs. (76)–(77). To do this, we need the eigenvalues  $\lambda_j$  of the transport matrix  $K - i\Omega$ , i.e., we must solve the secular equation (71). This secular equation can be expanded

$$\lambda^4 + b_3\lambda^3 + b_2\lambda^2 + b_1\lambda + b_0 = 0 \quad (78)$$

where

$$b_3 = k^2[\kappa' + \eta' + D'] + R' \quad (79a)$$

$$b_2 = k^2v_0^2 + (R' + D'k^2)[\kappa' + \eta']k^2 + \kappa'\eta'k^4 \quad (79b)$$

$$b_1 = k^2v_\infty^2(R' + D'k^2) + k^4v_T^2\kappa' + (R' + D'k^2)\kappa''k^4\eta' \quad (79c)$$

$$b_0 = (R' + D'k^2)v_{\infty T}^2k^4\kappa'' \quad (79d)$$

with

$$v_0^2 = \left(\frac{\partial p}{\partial \rho}\right)_{N,S,\Delta N} \quad (80a)$$

$$v_\infty^2 = \left(\frac{\partial p}{\partial \rho}\right)_{N,S,\Delta\mu/T} \quad (80b)$$

$$v_T^2 = \left(\frac{\partial p}{\partial \rho}\right)_{N,T,\Delta N} \quad (80c)$$

$$v_{\infty T}^2 = \left(\frac{\partial p}{\partial \rho}\right)_{N,T,\Delta\mu/T} \quad (80d)$$

$\rho$  is the mass density, the transport coefficients  $D'$ ,  $R'$ ,  $\kappa'$ , and  $\eta'$  are defined in Eqs. (66)–(69), and the thermal conductivity  $\kappa''$  is

$$\kappa'' = \kappa V \left(\frac{\partial T}{\partial E}\right)_{N,V,\Delta\mu/T} \quad (81)$$

The velocities  $v_0$ ,  $v_\infty$ ,  $v_T$ , and  $v_{\infty T}$  are all thermodynamic quantities whose significance is discussed below; they are rather complicated quantities when obtained directly from Eq. (69), and the details of the manipulations required in obtaining them in the form of Eqs. (80a)–(80d), as well as those required to obtain Eq. (81), are given in Appendix D.

Before looking in detail at the solutions to Eq. (78), it is interesting to study the imaginary part of the complex solutions, i.e., the sound velocities, under a set of very extreme conditions.

(1) If there is no reaction or dissipative transport, i.e., if  $R' = D' = 0$ , then the sound speed  $c$  is

$$c = v_0 \tag{82}$$

This is the speed of sound in a two-component system in which all transport properties, including chemical reactions, are slow; from Eq. (80a) we see that  $v_0$  is the "ordinary" adiabatic sound speed.

(2) If the reaction rate is infinitely rapid, i.e.,  $R' \rightarrow \infty$ , then

$$c = v_\infty \tag{83}$$

This is the speed of sound in a two-component system where the chemical reaction is so rapid that chemical equilibration ( $\Delta\mu = 0$ ) is instantaneous.

(3) If  $\kappa' \rightarrow \infty$ , and all relevant frequencies not dependent upon  $\kappa'$  are small, then

$$c = v_T \tag{84}$$

This is the speed of sound in the two-component system where thermal equilibrium is instantly reestablished, i.e.,  $\Delta T = 0$ .

(4) If  $R' \gg kc$  and  $k^2\kappa' \gg kc$ , but  $\eta'k^2 \ll kc$ , then

$$v = v_{\infty T} \tag{85}$$

This is the speed of sound in a two-component system in which instantaneous chemical and thermal equilibration is achieved, i.e.,  $\Delta\mu = 0$  and  $\Delta T = 0$ .

## 11. SPECTRA: LINEWIDTHS

The light scattering spectrum corresponding to the system under study consists of two Rayleigh lines and two Brillouin lines which are distorted because of dispersive contributions. Explicit expressions for the widths of the lines and the frequency shift of the Brillouin lines can readily be obtained, and comparison between theory and experiment can be carried out. The intensities of the lines are, however, very complicated expressions, dependent upon thermodynamic and transport quantities, and these can usefully be compared with experiment only in certain extreme limits. In order to obtain some insight, we will discuss the intensities only under these extreme conditions, but it should be remembered that in dealing with actual spectra, a more detailed and involved analysis may be necessary.

We will assume that

$$ck \gg k^2\eta, k^2\kappa', k^2D' \quad (86)$$

a condition that almost always holds ( $c$  is the sound speed). Consequently, we retain terms linear in  $k^2\eta'$ ,  $k^2\kappa'$ ,  $k^2\kappa''$ , and  $k^2D'$ , but no higher order terms. We also assume that  $\delta_\infty^2$ ,  $\delta_T^2$ ,  $\delta_{\infty T}^2$  are all small and need only be retained through first order, where

$$\delta_\infty^2 = (v_0^2 - v_\infty^2)/v_0^2 \quad (87)$$

$$\delta_T^2 = (v_0^2 - v_T^2)/v_0^2 \quad (88)$$

$$\delta_{\infty T}^2 = (v_0^2 - v_{\infty T}^2)/v_0^2 \quad (89)$$

The reaction rate  $R'$  can take on a wide range of values, but we will limit the discussion to values of  $R'$  such that

$$R'\kappa' \ll c^2 \quad (90)$$

Approximate expressions for the sound speed  $c$  and sound absorption frequency  $\Gamma_s$  can readily be obtained under the conditions specified above:

$$\Gamma_s = \frac{\eta'k^2}{2} \left( 1 + \frac{R'^2}{v_0^2k^2} \right) + \frac{\delta_\infty^2}{2} \frac{v_0^2k^2R'}{v_0^2k^2 + R'^2} \quad (91)$$

$$c^2 = v_0^2 - \frac{v_0^2R'^2\delta_\infty^2}{v_0^2k^2 + R'^2} + R'\eta' \quad (92)$$

The most interesting aspects of these equations are the  $k$  dependence and the  $R'$  dependence. For slow reactions, i.e., for  $v_0k \gg R'$ , one finds

$$\Gamma_s = \frac{1}{2}\eta'k^2 \quad (93)$$

$$c^2 = v_0^2 \quad (94)$$

These yield the well-known Brillouin linewidths  $\Gamma_s$  and frequency shift  $\pm kv_0$  characteristic of unreacting liquids. For fast reactions, i.e.,  $R' \approx ck$ , both the sound speed and sound absorption frequency exhibit a dependence upon  $R'$ ; the dependence of  $\Gamma_s$  upon  $R'$  is particularly pronounced.

Expressions for the widths of the two Rayleigh lines must be considered separately in various limits. For slow reactions,  $R' \ll ck$ , the widths are

$$\begin{aligned} 2\Gamma_\pm &= (R' + k^2D')(1 - \delta_\infty^2) + \kappa'k^2(1 - \delta_T^2) \\ &\pm \left\{ [(R' + k^2D')(1 - \delta_\infty^2) - \kappa'k^2(1 - \delta_T^2)]^2 \right. \\ &\quad \left. - 4(R' + k^2D')\kappa''k^2 \left( 1 - \frac{\kappa}{\kappa''} \frac{v_\infty^2 v_T^2}{v_0^4} \right) \right\}^{1/2} \end{aligned} \quad (95)$$

If the reaction is very slow,  $R' \ll \kappa'k^2$ , then

$$\Gamma_R = R' + k^2 D' \quad (96)$$

$$\Gamma_T = \kappa'k^2 \quad (97)$$

where  $\Gamma_R$ , the width of the “reaction line,” is the (+) solution in Eq. (95) and  $\Gamma_T$ , the width of the “thermal conduction” line, is the other solution. These are well-known results.<sup>(17,18)</sup> If the reaction rate is somewhat faster, comparable to the rate of thermal conduction, then  $R' \approx \kappa'k^2$  and we have what might be called the “degenerate case.” In this case the interaction between thermal conduction and the chemical reaction is very strong, and the two Rayleigh Lorentzians not only have comparable widths but they also both arise from chemical and thermal effects.<sup>(6,17,18)</sup>

For rapid reactions ( $R' \gg \kappa'k^2$ ),  $\Gamma_T$  once again becomes a pure thermal mode, but it differs slightly from the expression in Eq. (97):

$$\Gamma_T = \kappa''k^2 \quad (98)$$

where  $\kappa''$  is defined in Eq. (81).  $\Gamma_R$  becomes

$$\Gamma_R = (R' + k^2 D')[1 - (2R'/v_0^2)\eta'] \quad (99)$$

In this limit we should neglect the  $D'$  term, but we have kept it because Eq. (99) then reduces properly to the slow reaction limit, Eq. (96).

We see that away from the degenerate limit,  $\Gamma_T$  is a thermal mode with a  $k^2$  dependence, whereas  $\Gamma_R$  is a reaction mode with an  $R' + k^2 D'$  dependence. However, the situation is more complicated for the degenerate case.

These eigenvalues correspond to those obtained by Mountain,<sup>(21)</sup> but for fast reactions they differ from those given by Weinberg and Oppenheim.<sup>(13)</sup> The latter authors made use of a very strict  $k$  expansion and  $R'$  expansion and so did not retain the  $(v_0 k^2 + R'^2)$  denominators. The same is true of the related theory of rotational motion presented by Gershon and Oppenheim.<sup>(33)</sup>

## 12. SPECTRA: INTENSITIES

The intensities of the four lines depend upon a host of thermodynamic factors as well as upon  $\Delta\alpha$  and  $\alpha$  [see Eq. (76)]. We shall make estimates of the relative intensities of each line arising from each correlation function, i.e., the  $\Phi_j^{(ab)}$  for each  $j$  in Eq. (76). By the straightforward but lengthy procedure indicated in Eq. (77), one finds that the intensity factors  $\Phi_j^{(ab)}$  are

$$\begin{aligned} \Phi_j^{(ab)} = & \lambda_j^3 + \lambda_j^2 [R_{ab} + (D_{ab} + \kappa' + \eta')k^2] \\ & + \lambda_j [k^2 v_{ab}^2 + (R_{ab} + D_{ab} k^2)(\eta' + \kappa_{ab}) + \kappa' \eta'] \\ & + [(R_{ab} + D_{ab} k^2)k^2 v_{abR}^2 + \kappa' k^2 v_{abR}^2 \\ & + (R_{ab} + D_{ab} k^2)\kappa_{ab} \eta'] \end{aligned} \quad (100)$$

where  $(ab)$  represents  $(NN)$ ,  $(N \Delta N)$ ,  $(\Delta N, N)$ , or  $(\Delta N \Delta N)$ ; the  $v_{ab}$  are thermodynamic quantities with dimensions of speeds; the  $D_{ab}$ ,  $R_{ab}$ , and  $\kappa_{ab}$  are transport quantities related to  $D'$ ,  $R'$ , and  $\kappa'$  introduced in Eqs. (65)–(67). The  $v_{ab}$ ,  $v_{ab\kappa}$ ,  $v_{abR}$ ,  $D_{ab}$ ,  $R_{ab}$ , and  $\kappa_{ab}$  are given in Appendix E.

In the degenerate case,  $\kappa'k^2 \approx R'$ , and the two Rayleigh lines have comparable intensities. Here we shall exclude this degenerate case and obtain expressions for the relative intensities  $[\phi_j^{(ab)}/\Lambda_j]$ , where

$$\Lambda_j = (-\lambda_j + \lambda_{j'})(-\lambda_j + \lambda_{j''})(-\lambda_j + \lambda_{j'''}) \quad (101)$$

for all other cases. We shall make the assumption that all the velocities are large in the sense that

$$vk \gg \kappa'k^2, \kappa''k^2, \eta'k^2 \quad (102)$$

for all the  $v$ 's, i.e., for  $v_{ab\kappa}$ ,  $v_{abR}$ , and  $v_{ab}$  and for all relevant differences of these  $v$ 's; wherever such combinations of velocities do not obey the inequality in (102), they should be neglected but their retention introduces insignificant contributions. We still assume that  $\delta_{\infty}^2$ ,  $\delta_T^2$ , and  $\delta_{\infty R}^2$  are small compared to unity. Since so many different thermodynamic quantities enter into the intensity expressions, it is unlikely that quantitative interpretations of the intensities will be forthcoming in the near future.

In the very slow reaction limit ( $R' \ll k^2\kappa'$ ,  $k^2\eta'$ ), the intensity factor is

$$\Phi_R^{(ab)}/\Lambda_R = f_{ab}v_{ab\kappa}^2/v_0^2 \quad (103a)$$

$$\Phi_T^{(ab)}/\Lambda_T = (v_{ab}^2 - f_{ab}v_{ab\kappa}^2)/v_0^2 \quad (103b)$$

The  $f_{ab}$  are dimensionless thermodynamic quantities defined in Appendix E. In the fast reaction limit

$$\Phi_R^{(ab)}/\Lambda_R = (v_{ab}^2 - g_{ab}v_{abR}^2)k^2/(k^2v_0^2 + R'^2) \quad (104a)$$

$$\Phi_T^{(ab)}/\Lambda_T = g_{ab}v_{abR}^2/v_0^2 \quad (104b)$$

where the  $g_{ab}$  are also dimensionless thermodynamic quantities defined in Appendix E. If  $a = N$ , then  $f_{ab} = g_{ab} = 1$ . In the approximation used here, the thermal Rayleigh line has intensity factors  $[\Phi_T^{(ab)}/\Lambda_T]$  that are independent of  $k$  and independent of reaction rate  $R'$ , both for slow and fast rates, although it clearly does have an  $R'$  and  $k$  dependence in the degenerate regime. The intensity factors  $[\Phi_R^{(ab)}/\Lambda_R]$  for the reaction line are independent of  $k$  and  $R'$  for slow reactions, but depend upon both  $k$  and  $R'$  for fast reactions; they decrease with increasing  $R'$  at large  $R'$ ; for  $R' < kv_0$  they increase with increasing  $k$  but for  $R' \gg kv_0$ , they are independent of  $k$ .

Next we turn to the intensity of the Brillouin lines. The “normal” Lorentzian contributions are

$$\text{Re} \frac{\Phi_s^{(ab)}}{\Lambda_s} = \frac{v_0^2k^2[1 - (v_{ab}^2/v_0^2)] + g_{ab}R'^2[1 - (v_{abR}^2/v_0^2)]}{2(v_0^2k^2 + R'^2)} \quad (105)$$

For slow reactions

$$\operatorname{Re}(\Phi_s^{(ab)}/\Lambda_s) = \frac{1}{2}[1 - (v_{ab}^2/v_0^2)] \quad (106)$$

Thus for slow reactions the intensity is independent of  $k$  and  $R'$ ; for  $R'$  comparable to  $v_0k$ , the intensity has a complicated  $k$  and  $R'$  dependence; for  $R'$  much faster than  $v_0k$ , it is again independent of  $R'$  and  $k$ . The dispersive Lorentzian for the Brillouin lines has intensity factors  $\operatorname{Im}(\Phi_{ss}^{(ab)}/\Lambda_s)$ , where

$$\operatorname{Im} \frac{\Phi_s^{(ab)}}{\Lambda_s} = -\frac{k\{R'[g_{ab}(v_0^2 - v_{abR}^2) - (v_0^2 - v_{abR}^2)] + \frac{1}{2}\eta'k^2(v_0^2 - v_{ab}^2)\}}{2v_0(R'^2 + v_0^2k^2)} \quad (107)$$

It is interesting to study the ratio  $(\operatorname{Im} \Phi_s^{(ab)})/(\operatorname{Re} \Phi_{ss}^{(ab)})$ , which is a measure of the “distortion” of the Brillouin lines:

$$\frac{\operatorname{Im} \Phi_s^{(ab)}}{\operatorname{Re} \Phi_s^{(ab)}} = -\frac{v_0k\{R'[g_{ab}(v_0^2 - v_{abR}^2) - (v_0^2 - v_{ab}^2)] + \frac{1}{2}\eta'k^2(v_0^2 - v_{ab}^2)\}}{v_0^2k^2(v_0^2 - v_{ab}^2) + g_{ab}^2R'^2(v_0^2 - v_{abR}^2)} \quad (108)$$

For slow reactions, this ratio is linear in  $k$  with slope  $-\eta'/2v_0$ . For very fast reactions the ratio is also linear in  $k$  with slope

$$-(v_0/R')[1 - (v_0^2 - v_{ab}^2)g_{ab}^{-1}(v_0^2 - v_{abR}^2)^{-1}]$$

For reactions such that  $R'$  and  $kv_0$  are comparable, the ratio is linear in  $k$  for small  $k$  but turns around and decreases with increasing  $k$  at large  $k$ .

The four  $(ab)$  contributions  $\phi_j^{(ab)}$  for each  $j$  line all have the same functional  $k$  and  $R'$  dependences, but because of the differences in thermodynamic coefficients, both the observed  $k$  and  $R'$  dependences and the relative contributions to each line from each correlation function may be different. The  $(NN)$  contributions are of particular interest since they are the only contributions if the two species have identical polarizabilities, i.e., if  $\Delta\alpha = 0$ . In this case, for small  $R'$ ,

$$\frac{\Phi_R^{(NN)}}{\Lambda_R} = \rho \left( \frac{\partial p}{\partial \Delta N} \right)_{N,T,V} \frac{\Delta N}{v_0^2} \quad (109)$$

This is a small quantity since it is proportional to a concentration compressibility which is presumably small compared to the ordinary adiabatic compressibility  $v_0^2$ . The corresponding  $(\Delta N, \Delta N)$  contribution is

$$\frac{\phi_R^{(\Delta N \Delta N)}}{\Lambda_R} = \left( \frac{\partial p}{\partial \rho} \right)_{\Delta N, T, V} \left[ \left( \frac{\partial \Delta N}{\partial N} \right)_{\Delta \mu/T, E, V} \left( \frac{\partial N}{\partial \Delta N} \right)_{\mu, T, V} \right] \quad (110)$$

The numerator should be larger in this case. Hence the  $(\Delta N \Delta N)$  contribution to the reaction Rayleigh line should be larger than that of the  $(NN)$  correlation function, provided, of course, that  $\Delta\alpha$  and  $\alpha$  are comparable. The  $(NN)$  contribution is the Mountain line.<sup>(21)</sup> Similar arguments hold for the various lines in all limits and for the cross-correlations as well.

### 13. COMMENTS

One should note that if the polarizabilities of the two species are identical,  $\Delta\alpha = 0$ , and only the first of the three terms in Eq. (76) is nonvanishing. Even in this case, however, a fourth line, over and above the usual Rayleigh-Brillouin triplet, is present, and the half-width of this fourth line is dependent upon the rate  $R$  of the chemical reaction. This case is quite identical with that discussed by Mountain,<sup>(21)</sup> except that he neglected the dispersive contributions to the Brillouin lines, and that discussed by Weinberg and Oppenheim<sup>(13)</sup>; the fourth or  $\Gamma_R$  line is often called the Mountain line. In our notation the Mountain line arises because of the introduction of the fourth variable, the concentration variables  $\Delta N$ , but if  $\Delta\alpha = 0$ , it acts as a secondary variable, that is, it does not appear directly in the expression for the spectrum in Eq. (3). On the other hand, if  $\Delta\alpha \neq 0$ , the fourth line enters not only through  $\Delta N$  as a secondary variable, but also with  $\Delta N$  acting directly as a primary variable in the expression for the spectrum in Eq. (3). It is important to note that in this latter case the intensity of the reaction or concentration line with width  $\Gamma_R$  is not merely proportional to  $(\Delta\alpha)^2$  but also has contributions proportional to  $\alpha \Delta\alpha$  (cross-correlations) and contributions proportional to  $\alpha^2$  (Mountain line). Fortunately, these results indicate that rates of reaction  $\Gamma_R$  can be determined even if  $\Delta\alpha = 0$ .

If the degenerate condition,  $R' \approx \kappa'k^2$ , holds, the Rayleigh linewidths  $\Gamma_{\pm}$  depend both upon thermal conduction and reaction rates; we must use the complete expression in Eq. (95) for the linewidths of the two Rayleigh lines. In this case, the rate of reactive decay is strongly dependent upon the rate of thermal conduction. This means that the rate at which reaction takes place depends strongly upon the rate at which heat flows away from or toward the reacting volume element.

Whereas Weinberg and Oppenheim<sup>(13)</sup> have chosen the fourth variable to be the internal energy, a reasonable choice for the study of vibrational relaxation, we have been forced to consider a concentration variable such as  $\Delta N$  as our fourth variable since it is a much more natural one for discussing chemical reactions. In our notation, as given in Eqs. (18)–(20), Weinberg and Oppenheim's variable is  $[\epsilon_A \Delta_j^{(A)} + \epsilon_B \Delta_j^{(B)}]$ . Thus their currents are also given by equations analogous to Eqs. (19)–(21) with the 2 in Eq. (20) replaced by  $(\epsilon_A - \epsilon_B)$ , and  $\Delta_j^{(A)}$  and  $\Delta_j^{(B)}$  in Eq. (21) replaced by  $\epsilon_A \Delta_j^{(A)}$  and  $-\epsilon_B \Delta_j^{(B)}$ , respectively. For the one-component vibrational problem the two theories should give very similar results. For a two-component system with  $\Delta\alpha \neq 0$ , the concentration variable  $\Delta N$  is conserved in the absence of chemical reactions and must therefore be treated as a fourth, slowly varying relevant quantity; furthermore, it enters directly as a primary variable into the expression for  $I(\omega)$ .



As we mentioned in the introduction, Mountain, in his hydrodynamic theory, introduces a time-dependent viscosity instead of a fourth slow variable. Sutherland and Deutch's<sup>(10)</sup> treatment is a hydrodynamic equivalent of our procedures, but they carry out calculations for nonreacting two-component liquids with an internal degree of freedom. Salsburg *et al.*<sup>(17)</sup> have carried out calculations starting with equations of irreversible thermodynamics and applied them, in less detail, to reactions of greater complexity. Kapral *et al.*<sup>(30)</sup> have followed a similar procedure but have not included the conserved variables.

We note again that small differences do exist between molecular theories in which local field fluctuations are neglected and the molecular polarizability is assumed constant and thermodynamic theories in which the dielectric constant and the internal relaxation mode are functions of both density and temperature. (See Refs. 9, 10, 21.)

## APPENDIX A. EVALUATION OF $\sigma^{(e)}$

We wish to obtain the expression in Eq. (23) for energy flux density  $\sigma^{(e)}$ , defined in Eqs. (22) and (23). We first take the time derivative of  $E(\mathbf{k}, t)$  defined in Eq. (14),

$$\dot{E}(\mathbf{k}, t) = \sum_j i\mathbf{k} \cdot \mathbf{q}_j [\mathcal{E}_j] \exp i\mathbf{k} \cdot \mathbf{q}_j + \sum_j \frac{d\epsilon_j}{dt} \exp i\mathbf{k} \cdot \mathbf{q}_j \quad (\text{A.1})$$

where

$$\mathcal{E}_j = (p_j^2/2m) + \frac{1}{2} \sum_{j' \neq j} U_{jj'} + \epsilon_j \quad (\text{A.2})$$

In this expression the internal energy  $\epsilon_j$  is a function of the internal coordinate  $\xi_j$  and momentum  $\pi_j$  of the  $j$ th molecule, i.e.,  $\epsilon_j(\xi_j, \pi_j)$ . The potential energy  $U_{jj'}$  is a function of  $\mathbf{q}_{jj'}$  and of  $\xi_j$ , i.e.,  $U_{jj'}(q_{jj'}, \xi_j)$ . Now consider  $\mathcal{E}_j$ :

$$\begin{aligned} \dot{\mathcal{E}}_j = & \left\{ \frac{\mathbf{p}_j \cdot \dot{\mathbf{p}}_j}{m} + \frac{1}{2} \sum_{j'} \left[ \dot{\mathbf{q}}_j \cdot \nabla_j U_{jj'} + \dot{\mathbf{q}}_{j'} \cdot \nabla_{j'} U_{jj'} \right. \right. \\ & \left. \left. + \dot{\xi}_j \frac{\partial U_{jj'}}{\partial \xi_j} + \dot{\xi}_{j'} \frac{\partial U_{jj'}}{\partial \xi_{j'}} \right] + \frac{\partial \epsilon_j}{\partial \xi_j} \dot{\xi}_j + \frac{\partial \epsilon_j}{\partial \pi_j} \dot{\pi}_j \right\} \end{aligned} \quad (\text{A.3})$$

where  $\nabla_j$  is the gradient operator corresponding to  $\mathbf{q}_j$ . From Hamilton's equations of motion we have

$$\dot{\pi}_j = -\frac{\partial \epsilon_j}{\partial \xi_j} - \frac{1}{2} \sum_{j' \neq j} \left( \frac{\partial U_{jj'}}{\partial \xi_j} + \frac{\partial U_{j'j}}{\partial \xi_j} \right); \quad \dot{\xi}_j = \frac{\partial \epsilon_j}{\partial \pi_j} \quad (\text{A.4})$$

$$\dot{\mathbf{p}}_j = -\nabla_j \sum_{j'} U_{jj'}; \quad \dot{\mathbf{q}}_j = \mathbf{p}_j/m \quad (\text{A.5})$$

If we substitute Eqs. (A.4) and (A.5) into (A.3) and note that  $U_{jj'} = U_{j'j}$  and

$$\partial U_{jj'}/\partial \xi_j = \partial U_{jj'}/\partial \xi_{j'} \quad (\text{A.6})$$

then we obtain

$$\phi_j = \frac{1}{2m} \sum_{j'} [-\mathbf{p}_j \cdot \nabla_j U_{jj'} + \mathbf{p}_{j'} \cdot \nabla_{j'} U_{jj'}] - \frac{1}{2} \sum_{j'} \frac{\partial U_{jj'}}{\partial \xi_j} (\xi_j - \xi_{j'}) \quad (\text{A.7})$$

Next we substitute Eq. (A.7) into the second term in Eq. (A.1),

$$\begin{aligned} \sum_j \phi_j \exp i\mathbf{k} \cdot \mathbf{q}_j &= \frac{1}{4m} \sum_{j,j'} \left\{ [\mathbf{p}_{j'} \cdot \nabla_{j'} U_{jj'} - \mathbf{p}_j \cdot \nabla_j U_{jj'}] \exp i\mathbf{k} \cdot \mathbf{q}_j \right. \\ &\quad + [\mathbf{p}_j \cdot \nabla_j U_{jj'} - \mathbf{p}_{j'} \cdot \nabla_{j'} U_{jj'}] \exp i\mathbf{k} \cdot \mathbf{q}_{j'} \left. \right\} \\ &\quad - \frac{1}{4} \sum_{j,j'} \left\{ \left[ \frac{\partial U_{jj'}}{\partial \xi_j} (\xi_j - \xi_{j'}) \right] \exp i\mathbf{k} \cdot \mathbf{q}_j \right. \\ &\quad \left. + \left[ \frac{\partial U_{jj'}}{\partial \xi_{j'}} (\xi_{j'} - \xi_j) \right] \exp i\mathbf{k} \cdot \mathbf{q}_{j'} \right\} \quad (\text{A.8}) \end{aligned}$$

We note that

$$\nabla_j U_{jj'} = -\nabla_{j'} U_{jj'} \quad (\text{A.9})$$

Since  $U_{jj'}$  is short range, for small  $k$  we can expand  $\exp i\mathbf{k} \cdot \mathbf{q}_{j'}$ , and Eq. (A.8) becomes

$$\begin{aligned} \sum_j \phi_j \exp i\mathbf{k} \cdot \mathbf{q}_j &= \frac{1}{4} \sum_{j,j'} (i\mathbf{k} \cdot \mathbf{q}_{j'}) (\exp i\mathbf{k} \cdot \mathbf{q}_j) \\ &\quad \times \left[ \frac{1}{m} (\mathbf{p}_j + \mathbf{p}_{j'}) \cdot \nabla_j U_{jj'} + \frac{\partial U_{jj'}}{\partial \xi_j} (\xi_{j'} - \xi_j) \right] \quad (\text{A.10}) \end{aligned}$$

Equation (A.10) combined with Eqs. (A.1) and (A.2) yields Eq. (23).

## APPENDIX B. EVALUATION OF ZERO TIME CORRELATION FUNCTIONS

We present a derivation of the expressions used to express zero time correlation functions as thermodynamic derivatives, i.e., we derive Eqs. (34)–(37).

At equilibrium, in the absence of any external perturbations, the distribution function  $\rho_0$  for a system in a grand canonical ensemble is

$$\rho_0 = \exp -\beta(Ve - V\mu_A n_A - V\mu_B n_B) \quad (\text{B.1})$$

where  $e$  is the energy density for the system,  $V$  its volume,  $\beta = (k_B T)^{-1}$ ,  $T$  the

equilibrium temperature,  $\mu_\gamma$  the chemical potential, and  $n_\gamma$  the number density of the  $\gamma$ th species. The quantities  $T$  and  $\mu_\gamma$  are statistical quantities independent of the phase point variables  $p_j$  and  $q_j$ , the momentum and position of the  $j$ th particle. In the absence of external perturbations the system is uniform, and  $T$  and  $\mu_\gamma$  are constants. The quantities  $n_\gamma$  and  $e$  are functions of the phase point variables; since the system is uniform, both  $n_\gamma$  and  $e$  are independent of the space point  $\mathbf{R}$ , i.e., of position within the sample.

If we apply a set of small external perturbations to the system and allow the system to attain local equilibrium at each point  $\mathbf{R}$ , then the new distribution function has the form

$$\rho = \exp\left\{-\beta \int d\mathbf{R} \left[ e(\mathbf{R}) - \sum_j \mathbf{p}_j \delta(\mathbf{R} - \mathbf{q}_j) \cdot \overline{\mathbf{U}}(\mathbf{R}) + \frac{1}{2} \sum_j m_j \delta(\mathbf{R} - \mathbf{q}_j) \overline{U}(\mathbf{R})^2 - \mu_A(\mathbf{R}) n_A(\mathbf{R}) - \mu_B(\mathbf{R}) n_B(\mathbf{R}) \right]\right\} [T/T(\mathbf{R})] \quad (\text{B.2})$$

where  $d\mathbf{R}$  is a three-dimensional volume element,  $\sum_j \mathbf{p}_j \delta(\mathbf{R} - \mathbf{q}_j)$  is the momentum density, and  $\sum_j m_j \delta(\mathbf{R} - \mathbf{q}_j)$  is the mass density at point  $\mathbf{R}$ ;  $\overline{\mathbf{U}}(\mathbf{R})$  is the average flow velocity of a small volume element at point  $\mathbf{R}$ , a volume element small compared to  $V$  but large compared to molecular dimensions. We assume that all the quantities in Eq. (B.2) are at *local equilibrium* and well defined in each small volume element specified by the position  $\mathbf{R}$ . In order to obtain Eq. (B.2), we note that the total internal energy density  $e_{\text{int}}(\mathbf{R})$  of a volume element at point  $\mathbf{R}$  moving with velocity  $\overline{\mathbf{U}}(\mathbf{R})$  is

$$e_{\text{int}}(\mathbf{R}) = \frac{1}{2} \sum_j m_j [(\mathbf{p}_j/m_j) - \overline{\mathbf{U}}(\mathbf{R})]^2 \delta(\mathbf{R} - \mathbf{q}_j) + \dots \quad (\text{B.3})$$

where the potential and intramolecular energies have not been explicitly indicated. If the right-hand side of Eq. (B.3) is expanded, one obtains

$$e_{\text{int}}(\mathbf{R}) = \frac{1}{2} \sum_j m_j \delta(\mathbf{R} - \mathbf{q}_j) \overline{U}(\mathbf{R})^2 - \sum_j \mathbf{p}_j \delta(\mathbf{R} - \mathbf{q}_j) \cdot \overline{\mathbf{U}}(\mathbf{R}) + \left[ \frac{1}{2} \sum_j \frac{1}{m_j} p_j^2 \delta(\mathbf{R} - \mathbf{q}_j) + \dots \right] \quad (\text{B.4})$$

We note that the quantity in brackets is the total energy density  $e(\mathbf{R})$ , whose Fourier transform is given in Eq. (14). The distribution function  $\rho$  depends upon  $e_{\text{int}}(\mathbf{R})$ ; thus we replace  $e$  in Eq. (B.1) by  $e_{\text{int}}(\mathbf{R})$  and we are then led to Eq. (B.2).

The quantities  $T/T(\mathbf{R})$ ,  $\overline{\mathbf{U}}(\mathbf{R})$ , and  $\mu_\gamma(\mathbf{R})$  in Eq. (B.2) are all statistical averages independent of the phase points  $\{q_j, p_j\}$ ; they are dependent upon the space point  $\mathbf{R}$  because the system, though at local equilibrium, is no longer

homogeneous. It is these quantities, which do not depend upon the internal variables of the system, that we associate with “external forces or perturbations” which are responsible for the distortion of the distribution function from that in Eq. (B.1) to that in Eq. (B.2). We will make a *linear approximation*; we assume that the external forces are small, i.e., that only terms linear in  $[T/T(\mathbf{R}) - 1]$ ,  $\overline{\mathbf{U}(\mathbf{R})}$ , and  $[\mu_\gamma(\mathbf{R}) - \mu_\gamma]$  need be retained. Therefore, we can neglect the  $U(\mathbf{R})^2$  terms in Eq. (B.2). In the context of this linear approximation, we can expand the distribution function  $\rho$  about  $\rho_0$ , retaining linear terms only:

$$\rho = \rho_0 \left\{ 1 + \beta \int d\mathbf{R} \left[ e(\mathbf{R}) \frac{\delta T(\mathbf{R})}{T} + \sum_j \mathbf{p}_j \cdot \delta(\mathbf{R} - \mathbf{q}_j) \cdot \overline{\mathbf{U}(\mathbf{R})} + n_A(\mathbf{R}) T \delta\left(\frac{\mu_A(\mathbf{R})}{T(\mathbf{R})}\right) + n_B(\mathbf{R}) T \delta\left(\frac{\mu_B(\mathbf{R})}{T(\mathbf{R})}\right) \right] \right\} \quad (\text{B.5})$$

where  $\delta Q$  represents the small changes in a quantity  $Q$  in going between the two ensembles discussed above.

Now we discuss the average value  $\overline{\mathcal{A}}(k)$  of a set of quantities  $\mathcal{A}(k)$  in the ensemble represented by the distribution function or density matrix  $\rho$  in Eq. (B.5):

$$\overline{\mathcal{A}}(k) = \text{Tr } \rho(\mathcal{A}k) \quad (\text{B.6})$$

From Eqs. (30), (31), and (11) we see that, provided we exclude  $k \neq 0$ , we can replace  $\mathcal{A}(k)$  in Eq. (B.6) by the fluctuations  $A(k)$  of these quantities:

$$\overline{A}(k) = \text{Tr } \rho A(k) \quad (\text{B.7})$$

We next substitute Eq. (B.5) into Eq. (B.7), taking account of Eqs. (30) and (32):

$$\overline{A}(k) = \frac{\beta}{V(2\pi)^3} \left[ \langle A(k) E^*(k) \rangle \frac{\delta T(k)}{T} + \langle A(k) i\mathbf{k} \cdot M \mathbf{U}^*(k) \rangle \frac{\mathbf{U}(k)}{ik} + \langle A(k) N_A^*(k) \rangle T \delta\left(\frac{\mu_A(k)}{T(k)}\right) + \langle A(k) N_B^*(k) \rangle T \delta\left(\frac{\mu_B(k)}{T(k)}\right) \right] \quad (\text{B.8})$$

where  $-i\mathbf{k} \cdot M \mathbf{U}(k)$  is defined in Eq. (13),  $\mathbf{U}(k)$  is both the average of  $\mathbf{U}(k)$  and the Fourier transform of  $\overline{\mathbf{U}(\mathbf{R})}$ ,  $\langle Q \rangle$  indicates  $\text{Tr } \rho_0 Q$ , an average over phase points. Note that  $\delta(\mu_A(k)/T(k))$  is a short-hand notation for

$$\delta(\mu_A(k)/T(k)) = \mu_A(k) T^{-1} - \mu_A T_0^{-2} T(k) \quad (\text{B.9})$$

where  $\mu_A$  and  $T$  are equilibrium quantities in the undisturbed system,  $\mu_A(\mathbf{R})$  and  $T(\mathbf{R})$  are corresponding quantities in the perturbed system, and  $\mu_A(k)$

and  $T(k)$  are Fourier transforms of the fluctuations  $\delta\mu_A(\mathbf{R})$  and  $\delta T(\mathbf{R})$ . In obtaining Eq. (B.8), note that

$$\begin{aligned} & \int \langle A(k)A^*(\mathbf{R}) \rangle \cdot \delta B(\mathbf{R}) d\mathbf{R} \\ &= \int \int \langle A(k)A^*(k') \rangle \frac{\exp(-i\mathbf{k}' \cdot \mathbf{R})}{(2\pi)^3} d\mathbf{k}' \delta B(\mathbf{R}) d\mathbf{R} \end{aligned} \quad (\text{B.10})$$

If we substitute Eq. (32) into (B.10), the right-hand side of Eq. (B.10) becomes  $\langle A(k)A^*(k) \rangle \mathbf{B}(k)/(2\pi)^3 V$ . Equation (B.8) is equivalent to Eq. (34) with  $A(k)$  given by Eq. (35) and  $\mathbf{B}(k)$  by Eq. (37).

Since the various time-independent correlation functions that enter into the transport theory can be related to derivatives with respect to the "external perturbations"  $\mathbf{B}$ , it is important to understand precisely what these quantities are. We note that the quantity  $T(k)$  is defined as

$$T(k) = \int \exp(i\mathbf{k} \cdot \mathbf{R}) \delta T(\mathbf{R}) d\mathbf{R} \quad (\text{B.11})$$

In obtaining this quantity, we have assumed local equilibrium such that the temperature  $T(\mathbf{R})$ , and hence the fluctuation  $\delta T(\mathbf{R})$ , are uniform over a small volume element  $v_k$ ; this volume element can then be defined by the relation

$$T(k) = v_k \delta T(\mathbf{R}) (2\pi)^3 \quad (\text{B.12})$$

In the limit of small  $k$ ,  $v_k$  approaches the volume  $V$  of the system and

$$\lim_{k \rightarrow 0} T(k) \rightarrow V \delta T (2\pi)^3 \quad (\text{B.13})$$

In this limit  $\delta T(\mathbf{R})$  is uniform over the entire system. Note that  $T(k)$  has the dimensions of a temperature times a volume. Similarly, at local equilibrium,  $\delta\mu_A(\mathbf{R})$  is uniform over the volume  $v_k$  and

$$\lim_{k \rightarrow 0} \mu_A(k) \rightarrow V \delta\mu_A (2\pi)^3 \quad (\text{B.14})$$

At a given value of  $k$ , we have local equilibrium in a fixed volume element  $v_k$ . It therefore follows that *all thermodynamic derivatives in the theory are taken at constant volume.*

## APPENDIX C. EQUIVALENCE OF HYDRODYNAMIC EQUATIONS

We wish to prove that the transport matrix in Eq. (69) gives rise to the usual transport equations obtained by irreversible thermodynamics. First we note that the Mori theory<sup>(29)</sup> yields transport equations for  $\overline{A(\omega)}$ , the instan-

taneous average of the half-frequency transform of  $A(t)$ , which are analogous to Eq. (25):

$$\overline{\dot{A}(k, \omega)} = -[K(k, \omega) - i\Omega(k)]\overline{A(k, \omega)} \quad (\text{C.1})$$

In the low-frequency and low- $k$  regime  $K(\omega) = K(0)$ . Equation (69) gives the transport matrix associated with the variables  $A = \{N, \Delta N, E, -i\mathbf{k}M \cdot \mathbf{U}\}$ . These are not the variables usually used in irreversible thermodynamics, so we must transform to customary variables such as  $N, c, T, p$ , where  $p$  is the pressure and  $c$  is the mole fraction.

From Eqs. (C.1) and (69) we can obtain the relation

$$\begin{aligned} -ik\overline{M\dot{U}(k)} = V k^2 \left[ \left( \frac{\partial p}{\partial N} \right)_{\Delta N, E, V} \overline{N(k)} + \left( \frac{\partial p}{\partial \Delta N} \right)_{N, E, V} \overline{\Delta N(k)} \right. \\ \left. + \left( \frac{\partial p}{\partial E} \right)_{N, \Delta N, V} \overline{E(k)} \right] + k^2 \eta' ik \overline{M\dot{U}(k)} \end{aligned} \quad (\text{C.2})$$

The term in brackets is the transform of the pressure fluctuation per unit volume  $[\delta p(z)/V]$  at constant volume; if this substitution is made, Eq. (C.2) becomes

$$\frac{\partial \bar{g}}{\partial t} = -\frac{\partial p}{\partial z} + \eta' \frac{\partial^2}{\partial z^2} \bar{g} \quad (\text{C.3})$$

where  $\bar{g}$  is the momentum density. This is the Navier–Stokes equation.<sup>(9)</sup> (All thermodynamic derivatives are at constant  $U$ .) Similarly, from Eqs. (69) and (C.1) we obtain

$$\overline{\dot{N}(k)} = +ik\overline{M\dot{U}(k)}/m \quad (\text{C.4})$$

the equation of continuity. In position space this equation becomes

$$\partial \bar{n} / \partial t = -\nabla \cdot \bar{\mathbf{g}} \quad (\text{C.5})$$

where  $\bar{n}$  is the number density.

We next combine the third line of Eq. (69) with Eqs. (67), (44), and (C.4):

$$\begin{aligned} \overline{\dot{E}(k)} = -k^2 V \kappa \left[ \left( \frac{\partial T}{\partial N} \right)_{\Delta N, E, V} \overline{N(k)} + \left( \frac{\partial T}{\partial \Delta N} \right)_{N, E, V} \overline{\Delta N(k)} \right. \\ \left. + \left( \frac{\partial T}{\partial E} \right)_{N, \Delta N, V} \overline{E(k)} \right] + \frac{VT}{Nm} \left( \frac{\partial p}{\partial T} \right)_{\mu/T, \Delta \mu/T, V} ik \overline{M\dot{U}(k)} \end{aligned} \quad (\text{C.6})$$

The term in brackets is the transform of the temperature fluctuation per unit volume at constant volume. In the expressions above,  $\overline{E(k)}$  is the Fourier transform of the total energy density and  $E$  is the total energy. In the thermo-

dynamic derivatives,  $U = 0$ , and in these quantities  $E$  is therefore the internal energy. From Eq. (D.3) we note that the last term on the right-hand side of Eq. (C.6) is equal to  $ikH\overline{U(k)}$ , the enthalpy flow into a fixed volume element (fixed  $k$ ).

Next we transform to position space:

$$\frac{\partial \bar{e}}{\partial t} = -\frac{H}{MV} \frac{\partial \bar{g}}{\partial z} + \kappa \frac{\partial^2 T}{\partial z^2} \quad (\text{C.7})$$

where  $\bar{e}$  is the energy density. This is one of the hydrodynamic equations, [see Eq. (86') of Ref. 9: Note that the corresponding equation in Ref. 10 makes use of  $T$  rather than  $\bar{e}$ ].

We consider the second line of Eq. (69) as well as Eqs. (65), (44), and (D.4); by procedures similar to those above, we obtain

$$\overline{\Delta \dot{N}(k)} = -(Dk^2 + R)(N/2k_B) \delta(\overline{\Delta\mu(k)/T(k)}) + ik \Delta N \overline{U(k)} \quad (\text{C.8})$$

where  $\delta(\overline{\Delta\mu(k)/T(k)})$  is defined in Eq. (B.9). But instead of  $\Delta N(k)$  we wish to use  $c(k)$ , the Fourier transform of the fluctuation of the mole fraction of component A,

$$c(k) = \int d\mathbf{R} \delta(\overline{n_A(\mathbf{R})n(\mathbf{R})^{-1}}) \exp(i\mathbf{k} \cdot \mathbf{R}) \quad (\text{C.9})$$

For small fluctuations, only the fluctuations are affected by the transformation, i.e.,  $\delta n(\mathbf{R})$  goes to  $N(k)$  but  $n(\mathbf{R})$  is a constant  $N/V$ . Thus

$$\Delta N(k) = (2N/V)c(k) + (\Delta N/N)N(k) \quad (\text{C.10})$$

and we can expand  $\delta(\overline{\Delta\mu(k)/T(k)})$  as

$$\begin{aligned} & \delta(\overline{\Delta\mu(k)/T(k)}) \\ &= \left( \frac{\partial(\overline{\Delta\mu/T})}{\partial T} \right)_{p,c,V} \overline{T(k)} + \left( \frac{\partial(\overline{\Delta\mu/T})}{\partial p} \right)_{T,c,V} \overline{p(k)} + \left( \frac{\partial(\overline{\Delta\mu/T})}{\partial c} \right)_{p,T,V} \overline{c(k)} \end{aligned} \quad (\text{C.11})$$

Next we substitute Eqs. (C.11), (C.10), and (C.4) into Eq. (C.8):

$$\begin{aligned} \frac{2N}{V} \overline{\dot{c}(k)} &= -(D_c k^2 + R_c) \frac{N}{2k_B} \left[ \overline{c(k)} + \left( \frac{\partial c}{\partial T} \right)_{p,V,\Delta\mu/T} \overline{T(k)} \right. \\ & \left. + \left( \frac{\partial c}{\partial p} \right)_{T,V,\Delta\mu/T} \overline{p(k)} \right] \end{aligned} \quad (\text{C.12})$$

where

$$\frac{R_c}{R} = \frac{D_c}{D} = \left( \frac{\partial \Delta\mu/T}{\partial c} \right)_{p,T,V} \quad (\text{C.13})$$

## APPENDIX D. THERMODYNAMIC EQUIVALENTS OF SOUND SPEED

The variables  $N$ ,  $\Delta N$ , and  $E$  are suitable variables for the microscopic-linear response approach to the present problem, but these quantities are not the most suitable variables for macroscopic treatments. Thus the thermodynamic derivatives in Eq. (69) are not familiar ones, and the eigenvalues of Eq. (69), if expressed in terms of these derivatives, are not very revealing. For example,  $v_0^2$ , where  $v_0$  is the slow reaction sound speed given in Eq. (80a), enters as a coefficient in Eq. (79b) and has the following form if obtained directly from Eq. (69):

$$v_0^2 = \frac{V}{m} \left[ \left( \frac{\partial p}{\partial N} \right)_{\Delta, N, E, V} + \frac{TV}{N} \left( \frac{\partial p}{\partial T} \right)_{\mu/T, \Delta\mu/T, V} \left( \frac{\partial p}{\partial E} \right)_{N, \Delta N, V} + 2 \frac{V}{N} \left( \frac{\partial p}{\partial \Delta\mu} \right)_{\mu, T, V} \left( \frac{\partial p}{\partial \Delta N} \right)_{N, E, V} \right] \quad (\text{D.1})$$

Equation (D.1) can, with a bit of thermodynamic manipulation, be reduced to Eq. (80a). To do this, we proceed as follows. The molecular chemical potentials  $\mu$  and  $\Delta\mu$  defined in Eqs. (38) and (39) are related to the Gibbs free energy  $G$  by the relation

$$G = \frac{1}{2}\mu N + \frac{1}{2}\Delta\mu \Delta N \quad (\text{D.2})$$

where  $N$  and  $\Delta N$  are defined in Eqs. (36) and (8): The corresponding Gibbs–Duhem equation yields

$$\left( \frac{\partial p}{\partial T} \right)_{\mu/T, \Delta\mu/T} = \frac{H}{TV} \quad (\text{D.3})$$

and

$$\left( \frac{\partial p}{\partial \Delta\mu} \right)_{\mu, T} = \frac{\Delta N}{2V} \quad (\text{D.4})$$

where  $H$  is the enthalpy.

Next we note that in our notation the first and second laws of thermodynamics are

$$dE = T dS - p dV + \frac{1}{2}\mu dN + \frac{1}{2}\Delta\mu d\Delta N \quad (\text{D.5})$$

From this we obtain

$$\left( \frac{\partial p}{\partial E} \right)_{N, \Delta N, V} = \frac{1}{T} \left( \frac{\partial p}{\partial S} \right)_{N, \Delta N, \rho} \quad (\text{D.6})$$

(Note that holding  $N$  and  $V$  constant is equivalent to holding  $N$  and  $\rho$  constant; also note that all thermodynamic derivatives are taken at constant



$U$ , mean flow speed.) It can readily be seen with the aid of Eq. (D.6) that

$$\left(\frac{\partial p}{\partial \Delta N}\right)_{N,E,V} = -\frac{1}{T} \left(\frac{\partial p}{\partial S}\right)_{N,\Delta N,\rho} \left(\frac{\partial E}{\partial \Delta N}\right)_{p,\rho,N} \quad (\text{D.7})$$

We next reexpress the first term in Eq. (D.1):

$$\begin{aligned} \frac{V}{m} \left(\frac{\partial p}{\partial N}\right)_{\Delta N,E,V} &= \left(\frac{\partial p}{\partial \rho}\right)_{N,\Delta N,S} + \left(\frac{\partial p}{\partial N}\right)_{\Delta N,\rho,S} \left(\frac{\partial N}{\partial \rho}\right)_{\Delta N,E,V} \\ &\quad - \left(\frac{\partial p}{\partial S}\right)_{N,\Delta N,\rho} \left(\frac{\partial S}{\partial \rho}\right)_{\Delta N,E,V} \end{aligned} \quad (\text{D.8})$$

If we go back to Eq. (D.5) and replace  $N$  by  $\rho V/m$ , where  $\rho$  and  $V$  are both variables, then we can readily show that

$$\left(\frac{\partial S}{\partial \rho}\right)_{\Delta N,E,V} = \frac{1}{2} \frac{\mu N}{\rho T} \quad (\text{D.9a})$$

$$\left(\frac{\partial E}{\partial \Delta N}\right)_{p,\rho,N} = \frac{1}{2} \Delta \mu + T \left(\frac{\partial S}{\partial \Delta N}\right)_{p,\rho,N} \quad (\text{D.9b})$$

We also see that

$$\left(\frac{\partial N}{\partial \rho}\right)_v = \frac{N}{\rho} \quad (\text{D.10})$$

$$\left(\frac{\partial p}{\partial N}\right)_{\Delta N,\rho,S} = -\left(\frac{\partial p}{\partial S}\right)_{\Delta N,\rho,N} \left(\frac{\partial S}{\partial N}\right)_{\Delta N,\rho,p} \quad (\text{D.11})$$

We substitute Eqs. (D.2)–(D.4) and (D.7)–(D.11) into Eq. (D.1):

$$\begin{aligned} v_0^2 &= \left(\frac{\partial p}{\partial \rho}\right)_{N,\Delta N,S} - \frac{1}{T\rho} \left(\frac{\partial p}{\partial S}\right)_{N,\Delta N,\rho} \\ &\quad \times \left[ -S + N \left(\frac{\partial S}{\partial N}\right)_{\Delta N,\rho,p} + \Delta N \left(\frac{\partial S}{\partial \Delta N}\right)_{N,\rho,p} \right] \end{aligned} \quad (\text{D.12})$$

The quantity in brackets vanishes and so Eq. (D.12) reduces to Eq. (80a).

Similarly,  $v_T$  obtained directly from Eq. (69), is

$$\begin{aligned} v_T^2 &= v_0^2 + \frac{V}{m} \left(\frac{\partial p}{\partial E}\right)_{N,\Delta N,V} \left[ -\frac{T^2}{2} \left(\frac{\partial \mu/T}{\partial T}\right)_{N,\Delta N,V} \right. \\ &\quad \left. - \frac{T^2 V}{N} \left(\frac{\partial p}{\partial \Delta \mu}\right)_{\mu,T,V} \left(\frac{\partial \Delta \mu/T}{\partial T}\right)_{N,\Delta N,V} - \frac{TV}{N} \left(\frac{\partial p}{\partial T}\right)_{\mu/T,\Delta \mu/T,V} \right] \end{aligned} \quad (\text{D.13})$$

We now prove that this expression reduces to that in Eq. (80c). To do this, we rewrite the thermodynamic laws in Eq. (D.5) in terms of the Helmholtz free energy  $A$ :

$$dA = -S dT - p dV + \frac{1}{2} \mu dN + \frac{1}{2} \Delta \mu d\Delta N \quad (\text{D.14})$$

It follows that

$$-\frac{1}{2} \left( \frac{\partial \mu}{\partial T} \right)_{N, \Delta N, V} = \left( \frac{\partial S}{\partial N} \right)_{\Delta N, T, V} \quad (\text{D.15})$$

$$-\frac{1}{2} \left( \frac{\partial \Delta \mu}{\partial T} \right)_{N, \Delta N, V} = \left( \frac{\partial S}{\partial \Delta N} \right)_{N, V, T} \quad (\text{D.16})$$

If  $N$  and  $V$  are constant, the density  $\rho$  is constant. Next, we see that

$$\left( \frac{\partial S}{\partial N} \right)_{\Delta N, T, V} = \left( \frac{\partial S}{\partial N} \right)_{\Delta T, \rho, T} + \frac{\rho}{N} \left( \frac{\partial S}{\partial \rho} \right)_{\Delta N, N, T} \quad (\text{D.17})$$

We substitute Eqs. (D.15)–(D.17), (D.3), (D.4), (D.6), and (80a) into Eq. (D.13), remembering that if  $N$  and  $V$  are held constant, we can equally well hold  $N$  and  $\rho$  constant:

$$\begin{aligned} v_T^2 = & \left( \frac{\partial p}{\partial \rho} \right)_{N, \Delta N, S} + \frac{1}{\rho T} \left( \frac{\partial p}{\partial S} \right)_{N, \Delta N, \rho} \left\{ \left( \frac{N\mu}{2} + \frac{\Delta N \Delta \mu}{2} \right) - H \right. \\ & \left. + T \left[ N \left( \frac{\partial S}{\partial N} \right)_{\Delta N, \rho, T} + \Delta N \left( \frac{\partial S}{\partial \Delta N} \right)_{N, \rho, T} \right] + T \rho \left( \frac{\partial S}{\partial \rho} \right)_{\Delta N, N, T} \right\} \end{aligned} \quad (\text{D.18})$$

This is equal to

$$v_T^2 = \left( \frac{\partial p}{\partial \rho} \right)_{N, \Delta N, S} + \left( \frac{\partial p}{\partial S} \right)_{N, \Delta N, \rho} \left( \frac{\partial S}{\partial \rho} \right)_{N, \Delta N, T} \quad (\text{D.19})$$

which in turn is equivalent to Eq. (80c).

We also consider  $v_\infty^2$  in Eq. (80b); if obtained directly from Eq. (69), this gives

$$\begin{aligned} v_\infty^2 = & \frac{V}{m} \left[ \left( \frac{\partial p}{\partial N} \right)_{\Delta N, E, V} - \left( \frac{\partial p}{\partial \Delta N} \right)_{N, E, V} \left( \frac{\partial(\mu/T)}{\partial(\Delta\mu/T)} \right)_{N, E, V} \right. \\ & + \frac{TV}{N} \left( \frac{\partial p}{\partial T} \right)_{\mu/T, \Delta\mu/T, V} \left( \frac{\partial p}{\partial E} \right)_{N, \Delta N, V} \\ & \left. - \frac{2V}{NT} \left( \frac{\partial p}{\partial \Delta N} \right)_{N, E, V} \left( \frac{\partial T}{\partial \Delta\mu/T} \right)_{N, E, V} \left( \frac{\partial p}{\partial T} \right)_{\mu/T, \Delta\mu/T, V} \right] \end{aligned} \quad (\text{D.20})$$

The derivative  $[\partial(\mu/T)/\partial(\Delta\mu/T)]_{NEV}$  can be evaluated by rewriting it as

$$\left( \frac{\partial \mu/T}{\partial \Delta \mu/T} \right)_{NEV} = \left( \frac{\partial \mu/T}{\partial \Delta N} \right)_{NEV} \left( \frac{\partial \Delta N}{\partial \Delta \mu/T} \right)_{NEV} \quad (\text{D.21})$$

making use of the identity in Eq. (44a), and then contracting the right-hand side of Eq. (D.20),

$$\left( \frac{\partial \mu/T}{\partial \Delta \mu/T} \right)_{NEV} = - \left( \frac{\partial \Delta N}{\partial N} \right)_{\Delta \mu/T, E, V} \quad (\text{D.22})$$

Similarly,

$$\left(\frac{\partial T}{\partial \Delta\mu/T}\right)_{NEV} = \left(\frac{\partial T}{\partial \Delta N}\right)_{NEV} \left(\frac{\partial \Delta N}{\partial \Delta\mu/T}\right)_{NEV} \quad (\text{D.23})$$

and by making use of Eq. (44c), we obtain

$$\left(\frac{\partial T}{\partial \Delta\mu/T}\right)_{NEV} = -\frac{1}{2} T^2 \left(\frac{\partial \Delta N}{\partial E}\right)_{\Delta\mu/T, N, V} \quad (\text{D.24})$$

If we substitute Eqs. (D.22), (D.24), and (D.3) into Eq. (D.20), we obtain

$$\begin{aligned} v_\infty^2 = & \frac{N}{\rho} \left[ \left(\frac{\partial p}{\partial N}\right)_{\Delta N, E, V} + \left(\frac{\partial \Delta N}{\partial N}\right)_{\Delta\mu/T, E, V} \left(\frac{\partial p}{\partial \Delta N}\right)_{N, E, \rho} \right] \\ & + \frac{H}{\rho} \left[ \left(\frac{\partial p}{\partial E}\right)_{N, \Delta N, \rho} + \left(\frac{\partial p}{\partial \Delta N}\right)_{N, E, \rho} \left(\frac{\partial \Delta N}{\partial E}\right)_{\Delta\mu/T, N, \rho} \right] \end{aligned} \quad (\text{D.25})$$

The first bracket equals  $(\partial p/\partial N)_{\Delta\mu/T, E, V}$  and the second bracket equals  $(\partial p/\partial E)_{N, \rho, \Delta\mu/T}$ . Next consider

$$\left(\frac{\partial p}{\partial \rho}\right)_{\Delta\mu/T, E, V} = \left(\frac{\partial p}{\partial \rho}\right)_{\Delta\mu/T, S, N} + \left(\frac{\partial p}{\partial S}\right)_{\Delta\mu/T, N, \rho} \left(\frac{\partial S}{\partial \rho}\right)_{\Delta\mu/T, E, N} - \frac{N}{\rho} \left(\frac{\partial p}{\partial N}\right)_{\Delta\mu/T, E, \rho} \quad (\text{D.26})$$

[This expression is obtained by first obtaining  $(\partial p/\partial \rho)_{\Delta\mu/T, E, N}$  and then expanding this quantity to obtain  $(\partial p/\partial \rho)_{\Delta\mu/T, S, N}$ .] The relations

$$\left(\frac{\partial p}{\partial N}\right)_{\Delta\mu/T, E, \rho} = -\left(\frac{\partial p}{\partial E}\right)_{\Delta\mu/T, \rho, N} \left(\frac{\partial E}{\partial N}\right)_{\Delta\mu/T, \rho, p} \quad (\text{D.27})$$

$$\left(\frac{\partial p}{\partial S}\right)_{\Delta\mu/T, N, \rho} \left(\frac{\partial S}{\partial \rho}\right)_{\Delta\mu/T, E, N} = -\left(\frac{\partial p}{\partial E}\right)_{\Delta\mu/T, S, N} \left(\frac{\partial E}{\partial \rho}\right)_{\Delta\mu/T, S, N} \quad (\text{D.28})$$

are also useful. We now substitute Eqs. (D.26)–(D.28) into Eq. (D.25):

$$v_\infty^2 = \left(\frac{\partial p}{\partial \rho}\right)_{\Delta\mu/T, \rho, N} + \frac{1}{\rho} \left(\frac{\partial p}{\partial E}\right)_{\Delta\mu/T, N, \rho} \left[ H - N \left(\frac{\partial E}{\partial N}\right)_{\Delta\mu/T, \rho, S} - \rho \left(\frac{\partial E}{\partial \rho}\right)_{\Delta\mu/T, N, S} \right] \quad (\text{D.29})$$

If we set  $V = Nm/\rho$  in Eq. (D.5) and let  $N$  and  $\rho$  be variables, we obtain the result

$$\left(\frac{\partial E}{\partial \rho}\right)_{\Delta\mu/T, N, S} = \frac{pV}{\rho} + \frac{1}{2} \Delta\mu \left(\frac{\partial \Delta N}{\partial \rho}\right)_{\Delta\mu/T, N, S} \quad (\text{D.30})$$

Since  $\Delta\mu/T$ ,  $p$ , and  $\rho$  are all intensive,

$$N \left(\frac{\partial E}{\partial N}\right)_{\Delta\mu/T, \rho, \rho} = E \quad (\text{D.31})$$

If we substitute Eqs. (D.30) and (D.31) into Eq. (D.29) and use the fact that at equilibrium  $\Delta\mu = 0$ , we obtain Eq. (80c).

$v_{\infty T}^2$  can be treated in similar fashion.

Finally, if obtained directly from Eq. (69),  $\kappa_{nn}$  in Eq. (81) is

$$\begin{aligned}\kappa_{nn} &= \kappa' \left[ 1 - \left( \frac{\partial T}{\partial \Delta\mu/T} \right)_{N,E,V} \left( \frac{\partial \Delta\mu/T}{\partial T} \right)_{N,\Delta N,V} \right] \\ &= \kappa' \left[ 1 - \left( \frac{\partial \Delta N}{\partial E} \right)_{N,\Delta\mu/T,V} \left( \frac{\partial E}{\partial \Delta N} \right)_{N,T,V} \right]\end{aligned}\quad (\text{D.32})$$

where we have used Eq. (D.23) and a similar relation for  $[\partial(\Delta\mu/T)/\partial T]_{N,\Delta N,V}$ . By reverting to the definition of  $\kappa'$  in Eq. (67), we get Eq. (81).

## APPENDIX E. FACTORS APPEARING IN EXPRESSIONS FOR INTENSITIES

By using techniques similar to those used in Appendix D, we have found expressions for the terms in Eq. (100):

$$v_{ab}^2 = \frac{V}{\rho} \left[ \left( \frac{\partial p}{\partial A_c} \right)_{E,V,A_a} \left( \frac{\partial p}{\partial B_c} \right)_{T,V,A_b} + T \left( \frac{\partial p}{\partial E} \right)_{N,\Delta N,V} \left( \frac{\partial p}{\partial T} \right)_{V,A_b,B_c} \right] \quad (\text{E.1})$$

$$v_{ab\kappa}^2 = \frac{V}{\rho} \left[ \left( \frac{\partial p}{\partial A_c} \right)_{T,V,A_a} \left( \frac{\partial p}{\partial B_c} \right)_{T,V,A_b} \right] \quad (\text{E.2})$$

$A_i$  is the  $i$ th variable [Eq. (35)] and  $B_i$  the conjugate thermodynamic potential [Eq. (37)]. The subscripts  $a$ ,  $b$ , and  $c$  are over  $N$  and  $\Delta N$  and  $c \neq a$ . We have

$$g_{ab} = \kappa_{ab}/\kappa'' \quad (\text{E.3})$$

where  $\kappa''$  is defined in Eq. (81):

$$g_{NN} = g_{\Delta NN} = g_{N\Delta N} = 1 \quad (\text{E.4})$$

and

$$g_{N\Delta N} = \left( \frac{\partial T}{\partial E} \right)_{N,\Delta} \left[ 1 - \left( \frac{\partial(\mu/T)}{\partial T} \right)_{\Delta N,\Delta\mu,V} \left( \frac{\partial T}{\partial(\mu/T)} \right)_{N,E,V} \right]^{-1} \quad (\text{E.5})$$

Furthermore,

$$f_{ab} = \frac{R_{ab} + D_{ab}k^2}{R' + D'k^2} \quad (\text{E.6})$$

$$f_{NN} = f_{N\Delta N} = f_{\Delta NN} = 1 \quad (\text{E.7})$$

and

$$\begin{aligned} \frac{R_{\Delta N \Delta N}}{R'} = \frac{D_{\Delta N \Delta N}}{D'} = & \left( \frac{\partial(\Delta\mu/T)}{\partial(\mu/T)} \right)_{\Delta N, T, V} \left( \frac{\partial(\mu/T)}{\partial(\Delta\mu/T)} \right)_{N, E, V} \\ & + \left( \frac{\partial(\Delta\mu/T)}{\partial T} \right)_{\Delta N, \mu, V} \left( \frac{\partial T}{\partial(\Delta\mu/T)} \right)_{N, E, V} \end{aligned} \quad (\text{E.8})$$

The expressions for  $v_{abR}^2$  are

$$v_{NNR}^2 = \frac{TV}{\rho} \left[ \left( \frac{\partial p}{\partial E} \right)_{N, \Delta\mu/T, V} \left( \frac{\partial p}{\partial T} \right)_{N, \Delta\mu/T, V} \right] \quad (\text{E.9})$$

$$v_{N\Delta NR}^2 = \frac{TV}{\rho} \left[ \left( \frac{\partial p}{\partial E} \right)_{N, \Delta\mu/T, V} \left( \frac{\partial p}{\partial T} \right)_{\Delta\mu/T, \Delta N, V} \right] \quad (\text{E.10})$$

$$\begin{aligned} v_{\Delta NNR}^2 = \frac{TV}{\rho} & \left[ \left( \frac{\partial p}{\partial E} \right)_{\Delta N, \mu, V} \left( \frac{\partial p}{\partial T} \right)_{\Delta\mu, N, V} \right] \\ & \times \left[ 1 - \left( \frac{\partial(\mu/T)}{\partial T} \right)_{N, \Delta\mu, V} \left( \frac{\partial T}{\partial(\mu/T)} \right)_{N, E, V} \right]^{-1} \end{aligned} \quad (\text{E.11})$$

$$\begin{aligned} v_{\Delta N\Delta NR}^2 = \frac{TV}{\rho} & \left[ \left( \frac{\partial p}{\partial E} \right)_{\Delta N, \mu, V} \left( \frac{\partial p}{\partial T} \right)_{\Delta\mu, \Delta N, V} \right] \\ & \times \left[ 1 - \left( \frac{\partial(\mu/T)}{\partial T} \right)_{\Delta N, \Delta\mu, V} \left( \frac{\partial T}{\partial(\mu/T)} \right)_{N, E, V} \right]^{-1} \end{aligned} \quad (\text{E.12})$$

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## REFERENCES

1. L. Landau and G. Placzek, *Physik Z. Sowjetunion* **5**:172 (1934).
2. R. D. Mountain, *Rev. Mod. Phys.* **38**:205 (1966); *J. Res. NBS* **70A**:207 (1966).
3. B. V. Felderhoff and I. Oppenheim, *Physica* **31**:1441 (1965).
4. E. Tong and R. C. Desai, *Phys. Rev. A* **2**:2129 (1970).
5. R. D. Mountain, *J. Res. NBS* **72A**:95 (1968).

6. R. D. Mountain and J. M. Deutch, *J. Chem. Phys.* **50**:1103 (1969).
7. L. Blum, *J. Chem. Phys.* **49**:1972 (1968).
8. L. Fishman and R. D. Mountain, *J. Phys. Chem.* **74**:2178 (1970).
9. R. H. Trimble and J. M. Deutch, *J. Stat. Phys.* **3**:149 (1971).
10. J. H. Sutherland and J. M. Deutch, *Chem. Phys.* **1**:447 (1973).
11. T. Keyes and D. Kivelson, *J. Chem. Phys.* **54**:1786 (1971). Erratum: *J. Chem. Phys.* **55**:986 (1972).
12. N. D. Gershon and I. Oppenheim, *Physica* **62**:198 (1972).
13. M. Weinberg and I. Oppenheim, *Physica* **61**:1 (1972).
14. R. C. Desai and R. Kapral, *Phys. Rev. A* **6**:2377 (1972).
15. N. D. Gershon and I. Oppenheim, *Physica* **71**:131 (1974).
16. C. Cohen, J. W. H. Sutherland, and J. M. Deutch, *Phys. Chem. Liquids* **2**:213 (1971).
17. L. Blum and Z. W. Salsburg, *J. Chem. Phys.* **48**:2292 (1968); **50**:1654 (1969); L. Blum, *J. Chem. Phys.* **51**:5024 (1969); **50**:17 (1969); D. L. Knirk and Z. W. Salsburg, *J. Chem. Phys.* **54**:1254 (1971).
18. B. J. Berne and H. L. Frisch, *J. Chem. Phys.* **47**:3675 (1967); B. J. Berne and R. Pecora, *J. Chem. Phys.* **50**:783 (1969); B. J. Berne, J. M. Deutch, J. T. Hynes, and H. L. Frisch, *J. Chem. Phys.* **49**:2864 (1968).
19. M. Huang and W. H. Swartz, *J. Chem. Phys.* **60**:1813 (1974).
20. R. Zwanzig, *J. Chem. Phys.* **43**:714 (1965).
21. R. D. Mountain, *J. Res. NBS* **70A**:207 (1966); **72A**:95 (1968).
22. W. S. Gornall, G. I. A. Stegeman, B. P. Stoicheff, R. H. Stohm, and V. Volterra, *Phys. Rev. Letters* **17**:297 (1966).
23. G. I. A. Stegeman and B. P. Stoicheff, *Phys. Rev. A* **7**:1160 (1973).
24. M. Dubois, P. Berge, and C. Laj, *Chem. Phys. Letters* **6**:227 (1970); P. Berge and M. Dubois, *C. R. Acad. Sci. (Paris)* **269**:842 (1969); *Phys. Rev. Letters* **26**:121 (1971); P. Berge, P. Calmettes, M. Dubois, and C. Laj, *Phys. Rev. Letters* **24**:89 (1970); I. M. Arefe'ev, B. D. Kopylovskii, D. ShMask, and I. L. Fabelinski, *Zh. Eksp. Teor. Fiz. Pis'ma* **5**:438 (1967) [English transl.: *Soviet Phys.—JETP Letters* **5**:355 (1967)]. M. J. Cardomone and D. P. Eastman, *J. Chem. Phys.* **59**:533 (1973). A. M. Jamieson and A. G. Walton, *J. Chem. Phys.* **58**:1054 (1973).
25. Y. Yeh and R. N. Keeler, *J. Chem. Phys.* **51**:1121 (1969); Y. Yeh, *J. Chem. Phys.* **52**:6218 (1970).
26. G. R. Alms, D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.* **59**:5321 (1973).
27. L. Blum and H. L. Frisch, *J. Chem. Phys.* **55**:1188 (1971); Y. Pomeau, *J. Chem. Phys.* **58**:293 (1973).
28. T. Keyes and D. Kivelson, *J. Chem. Phys.* **56**:1057 (1972).
29. H. Mori, *Prog. Theor. Phys. Japan* **33**:423 (1965).
30. W. Weinberg and R. Kapral, *J. Chem. Phys.* **53**:4409 (1970); R. Kapral, *J. Chem. Phys.* **56**:1842 (1972).
31. E. M. Simon, *J. Chem. Phys.* **54**:4738 (1971).
32. H. Mori, *Phys. Rev.* **112**:1829 (1958).
33. N. Gershon and I. Oppenheim, *Physica* **64**:247 (1973).